The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

A Study on Ozone Modification of Lignin in Alkali-Fiberized Wood

Thomas E. Lyse

June, 1979

A STUDY ON OZONE MODIFICATION OF LIGNIN IN ALKALI-FIBERIZED WOOD

A thesis submitted by

Thomas E. Lyse

B.S. 1974, University of Washington, Seattle

M.S. 1976, Lawrence University

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence University,
Appleton, Wisconsin

June, 1979

TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	3
Significance of the Problem	3
Background	3
Ozone	4
Ozone Reactions with Olefins	4
Ozone Reactions with Lignin	6
Model Studies	6
Summary — Ozone Reactions with Lignin Model Compounds	11
Isolated Lignin Studies	11
Proposed Reaction Mechanisms for Ozone Oxidation of Lignin	13
Ionic Mechanisms	13
Free-Radical Mechanisms	16
Summary of Ozone Reactions with Lignin	18
Ozone Reactions with Cellulose	19
Treatment of Wood Pulps with Ozone	20
Ozone Bleaching of Chemical Pulps	20
Effect of Ozone on Mechanical Pulps	22
Effect of Ozone on Wood	23
Ozone Pretreatment of Alkali-Fiberized Wood to Promote Reaction with Oxygen/Alkali	24
THESIS OBJECTIVE	26
EXPERIMENTAL APPROACH	27
Fourier Transform Infrared Spectroscopy	27
Difference Spectroscopy	27

RESULTS AND DISCUSSION 29

Ozone Oxidation of Fiberized Wood — Technical Aspects 29

Starting Material 29

Ozone Consumption in Reactions with Fiberized Wood 29

Effect of Ozonation on Fiberized Wood Yield 31

Delignification of Fiberized Wood with Ozone 33

Aromatic Content of Fiberized Wood Lignin 35

Proposed Mechanism for Ozone Degradation of Aromatic Rings in Lignin 37

Stoichiometry of Ozone-Lignin Reaction 39

Selectivity of Ozone-Lignin Reaction 42

Ozone Degradation of Fiberized Wood Carbohydrate 44

Lignin-Free Yield for Ozonated Fiberized Wood 44

Carbohydrate Content of Solubilized Material 45

Carbohydrate Content of Untreated and Ozonated Fiberized Wood 47

Cuene Viscosity of Untreated and Ozonated Fiberized Wood 48

Possible Mechanisms for Carbohydrate Solubilization 50

Effect of Ozone on Fiberized Wood Brightness 52

Summary — Technical Aspects of Ozone Oxidation of Fiberized Wood 54

Ozone Oxidation of Fiberized Wood — Effect on Specific Functional Groups 56

Methoxyl 56

Solubilized Methoxyl and Stoichiometry of Ozone-Methoxyl Reaction 59

Reaction Scheme for Solubilization of Methoxyl Groups in Ozonated Fiberized Wood Lignin 60

Methoxyl Content of Water-Soluble Fraction of Ozonated Fiberized Wood 60

Carboxyl 63

Formation of Carboxyl Groups in Ozonated Fiberized Wood 64

Mechanism for *in situ* Carboxyl Formation of Lignin and Carbohydrate Components of Ozonated Fiberized Wood 67

Magnitude of Carboxyl Production for the Ozone-Fiberized Wood Reaction 69

Partial Chemical Characterization of the Acidic, Water-Soluble Reaction Products 70

Carbonyl 73

Unconjugated Carbonyl 74

Unconjugated, Noncarboxyl Carbonyl Formation in Ozonated Fiberized Wood 76

Mechanistic Implications 78

Estimate of Increase in Unconjugated, Noncarboxyl Carbonyl Content of Ozonated Fiberized Wood as Compared to Untreated Wood 80

Conjugated Carbonyl 82

Mechanisms for Generation and Solubilization of Conjugated Carbonyl Groups in Ozonated Fiberized Wood Lignin 85

Estimate of Decrease in Conjugated, Noncarboxyl Carbonyl Content of Ozonated Fiberized Wood Lignin 87

Phenolic Hydroxyl 89

Use of FT-IR Difference Spectroscopy for Phenolic Hydroxyl Analysis 89

Methylation Technique for Estimate of Phenolic Hydroxyl Content in Fiberized Wood 91

Methylation of Untreated Fiberized Wood 92

Validity of Methylation Technique for Estimating Phenolic Hydroxyl Content of Fiberized Wood 94

Methylation of Ozonated Fiberized Wood 96

Calculation of Phenolic Hydroxyl Content of Untreated and Ozonated Fiberized Wood Based on Methylation Results 98

Proposed Mechanism for *in situ* Loss of Phenolic Hydroxyl Groups in Fiberized Wood Lignin 100

Active Oxygen 101

Mechanisms for Active Oxygen Formation in Ozonated Fiberized Wood 102

Ester and Lactone 103

Summary — Effect of Ozone Oxidation on Specific Functional Groups in Fiberized Wood 105

Methoxyl 105

Carboxyl 105

Unconjugated Carbonyl 105

Conjugated Carbonyl 106

Phenolic Hydroxyl 106

Active Oxygen 107

Ozone Oxidation of Fiberized Wood — As a Pretreatment for Oxygen/Alkali Pulping 107

CONCLUSIONS 110

EXPERIMENTAL 111

Preparation of Starting Material 111

Fiberized Wood Yield Determination 111

Acetone Extraction of Fiberized Wood 113

pH Adjustment of Extracted, Fiberized Wood 113

Experimental Apparatus 114

Calibration of Ozone Generator 114

Procedure for Calibration of Ozone Generator 114

Preparation of Fiberized Wood for Ozone Treatment 116

Reaction Conditions and Procedure for Ozone Treatment of Fiberized Wood 117

Hydrogen Peroxide Carry-over Experiment 117

Procedure 118

Procedure for Acid-Wash of Untreated Wood 119

Analytical Procedures 120

Surface Area 120

Calculation of Fiberized Wood Surface Area 121

Ozone Consumption 122

Active Oxygen 122

Klason Lignin 123

Acid-Soluble Lignin 123

Methoxyl 123

Carboxyl 124

Holocellulose Isolation 124

Viscosity 124

Carbohydrate 126

Brightness 129

Luminance Reflectance 129

Oxalic Acid 129

Phenolic Hydroxyl 130

Procedure for Methylation of Fiberized Wood 130

Procedure for Recovery of Water-Soluble Reaction Products 134

Preparation of Fiberized Wood for Infrared Analysis 134

Pellet Formation 134

Neutralization of Fiberized Wood Samples 135

Acidification of Fiberized Wood Samples 135

Procedure for Obtaining Infrared Spectra 135

Difference Spectra 136

Procedure for Measuring Absorbance of FT-IR Spectra 137

Transmission Spectra 137

Difference Spectra 137

Procedure for Calculating Normalized Spectra 138

SUGGESTIONS FOR FURTHER RESEARCH 139

ACKNOWLEDGMENTS 140

LIST OF ABBREVIATIONS 141

LITERATURE CITED 142

APPENDIX I. ADVANTAGES OF FOURIER TRANSFORM INFRARED SPECTROSCOPY 147

APPENDIX II. BAND ASSIGNMENTS FOR INFRARED ABSORPTION IN FIBERIZED WOOD 149

APPENDIX III. CHARACTERIZATION OF STARTING MATERIAL 150

APPENDIX IV. UNTREATED AND OZONATED FIBERIZED WOOD FT-IR TRANSMISSION SPECTRA 151

APPENDIX V. NEUTRALIZED FIBERIZED WOOD FT-IR TRANSMISSION SPECTRA 161

APPENDIX VI. ACIDIFIED FIBERIZED WOOD FT-IR TRANSMISSION SPECTRA 167

APPENDIX VII. OZONATED FIBERIZED WOOD FT-IR DIFFERENCE SPECTRA 173

APPENDIX VIII. OZONATED, NEUTRALIZED FIBERIZED WOOD FT-IR DIFFERENCE SPECTRA 186

APPENDIX IX. CALCULATION OF LIGNIN-FREE YIELD 191

APPENDIX X. EFFECT OF LIGNIN SOLUBILIZATION ON FIBERIZED WOOD BRIGHTNESS 192

APPENDIX XI. METHOXYL ASSOCIATED WITH LIGNIN IN FIBERIZED WOOD 193

APPENDIX XII. METHOXYL CONTENT OF RESIDUAL LIGNIN IN OZONATED FIBERIZED WOOD 194

APPENDIX XIII. METHOXYL CONTENT OF WATER-SOLUBILIZED MATERIAL 195

APPENDIX XIV. INFRARED SPECTRA OF ISOLATED REACTION PRODUCTS 196

APPENDIX XV. NEUTRALIZED FW MINUS ACIDIFIED FW FT-IR DIFFERENCE SPECTRA 199

APPENDIX XVI. INFRARED SPECTRA OF HOLOCELLULOSE ISOLATED FROM UNTREATED AND OZONATED FIBERIZED WOOD 205

APPENDIX XVII. INFRARED SPECTRUM OF LOBLOLLY PINE DIOXANE LIGNIN 209

APPENDIX XVIII. PHENOLIC HYDROXYL CONTENT OF FIBERIZED WOOD BASED ON METHYLATION RESULTS 211

SUMMARY

The ozone oxidation of alkali-fiberized loblolly pine (Pinus taeda) was investigated to elucidate the manner in which fiberized wood (FW) is modified by ozone treatment. This information will be of value in determining ozone's potential use in pulping and bleaching processes.

The experimental approach involved treatment of high-consistency FW with 1-7% ozone (based on o.d. FW). The untreated and ozonated FW was chemically characterized using analytical and FT-IR Difference spectroscopy techniques. Characterization included lignin, carbohydrate, and functional group analyses of FW samples and water-soluble reaction products. The results relating to the technical aspects of ozone oxidation of FW are summarized in the following paragraph.

Significant lignin solubilization was achieved, with up to 39% of the original lignin removed at 7% ozone consumption. Ozone was a selective oxidant with lignin being preferentially degraded and solubilized. The majority of the water-soluble reaction products were lignin-derived. Carbohydrate solubilization was minimal with lignin-free yields greater than 95%. There was no evidence for carbohydrate chain degradation in ozonated fiberized wood.

The results relating to the chemical aspects of ozone oxidation showed the aromatic rings in FW were degraded to water-soluble products. The extent of degradation was a function of ozone consumption. There was also evidence for limited (maximum of 20%) in situ modification of the ring structures. There was no modification of the methoxyl groups in the residual lignin of ozonated FW. One methoxyl group was removed from the FW with each lignin C-9 unit solubilized.

The unconjugated carbonyl content of FW increased upon ozonation. This increase was attributable to the formation of both noncarboxyl and carboxyl carbonyl functionalities. A small (20-50%) increase in the *in situ* carboxyl content of ozonated FW was found. *In situ* carboxyl formation did not appear to be a function of ozone consumption. A somewhat larger increase was noted for unconjugated, noncarboxyl carbonyl groups. It was estimated there were 2-4 times more noncarboxyl carbonyl groups in ozonated FW lignin as compared to untreated FW lignin. Their formation appeared to be a function of ozone consumption.

The majority (70-78%) of the ozone consumed by FW (at consumption levels of 3% or greater) resulted in carboxyl formation. Most of the carboxyl (63-97%) was incorporated into the water-soluble FW degradation products.

The conjugated carbonyl content of FW lignin decreased upon ozonation. About half as much conjugated, noncarboxyl carbonyl was present in the residual lignin of 7% ozonized FW as was present in untreated FW lignin.

Previous work has indicated formation of phenolic hydroxyl groups will aid oxygen/alkali delignification of wood. The phenolic hydroxyl content of FW decreased slightly upon ozonation, thus limited amounts of ozone will not promote this type of lignin activation.

Based on the above-mentioned results, it was concluded ozonation has a small modifying effect on the *in situ* lignin of fiberized wood. The majority of the lignin that reacted with ozone was degraded to water-soluble products containing carboxyl and carbonyl functionalities. The carbohydrate component of fiberized wood undergoes only slight degradation, and subsequent solubilization, upon ozone treatment.

INTRODUCTION

SIGNIFICANCE OF THE PROBLEM

With the ever-increasing emphasis on evironmental protection, the pulp and paper industry must look to new, nonpolluting, pulping and bleaching agents. Development of processes which eliminate, or at least reduce the use of sulfur-containing pulping chemicals and chlorine-containing bleaching agents are being sought. One solution to the problem is afforded through the use of oxygen and ozone for delignification agents since their use is less harmful to the environment.

Ozone is one of the strongest oxidizing agents known. It is currently being used in pilot-plant studies to bleach chemical pulps. Ozone treatment of mechanical pulps has been shown to increase both pulp brightness and strength (1-3). It also effectively reduces pitch problems in resinous wood systems (4). The use of ozone as a pretreatment in oxygen/alkali pulping processes, to increase lignin reactivity and reduce carbohydrate degradation, also shows promise (5).

In summary, ozone's current and most likely increasing use as a nonpolluting oxidant is of great importance to the pulp and paper industry. The ozone chemistry involved in wood systems is complicated and not well understood. This study is designed to provide much-needed information as to how lignin and fiberized wood are modified by ozone treatment.

BACKGROUND

The purpose of this section is to provide the reader with some background on the chemical nature of ozone and how it may react with lignin and cellulose. General information on ozone treatment of chemical and mechanical wood pulps,

and wood itself, is included. Ozone pretreatment of fiberized wood to increase lignin reactivity in oxygen/alkali pulping is also discussed.

OZONE

Ozone is one of the strongest oxidizing agents known, exceeded in electronegative oxidation potential only by F_2, F_2O, and the oxygen atom (6). Ozone is formed from oxygen in a strongly endothermic reaction and decomposes easily into molecular and atomic oxygen (7).

Most commonly, ozone is obtained by passing air or oxygen through a corona discharge. Some of the oxygen molecules are dissociated into oxygen atoms, which in turn combine with oxygen molecules to form ozone (6).

The ozone molecule is generally classified as a 1,3 dipole (see Fig. 1). In one resonance form, the central atom and one terminal atom possess full octets of electrons, while the other terminal oxygen atom has only a sextet of electrons. This electron deficiency in the terminal oxygens gives ozone an electrophilic character and is responsible for it's electrophilic attack on electron-rich substrates (6).

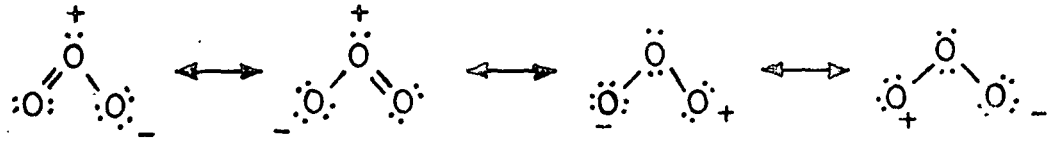

Figure 1. Resonance Forms of Ozone

OZONE REACTIONS WITH OLEFINS

The reaction of ozone with carbon-carbon double bonds has been throughly studied and a great deal of experimental data have been accumulated for this

particular reaction (7). Since lignin contains olefinic and aromatic bonds, a brief discussion of this work is relevant.

The ozonolysis reaction proceeds by a three-step mechanism proposed by Criegee (8). The Criegee mechanism of ozonolysis is outlined as follows.

The zwitterion serves as a reactive intermediate and can follow three separate pathways to produce reaction products. The most important pathway, from the standpoint of ozonolysis, is recombination of the zwitterion with the carbonyl fragment to form the final ozonide as shown in Fig. 2.

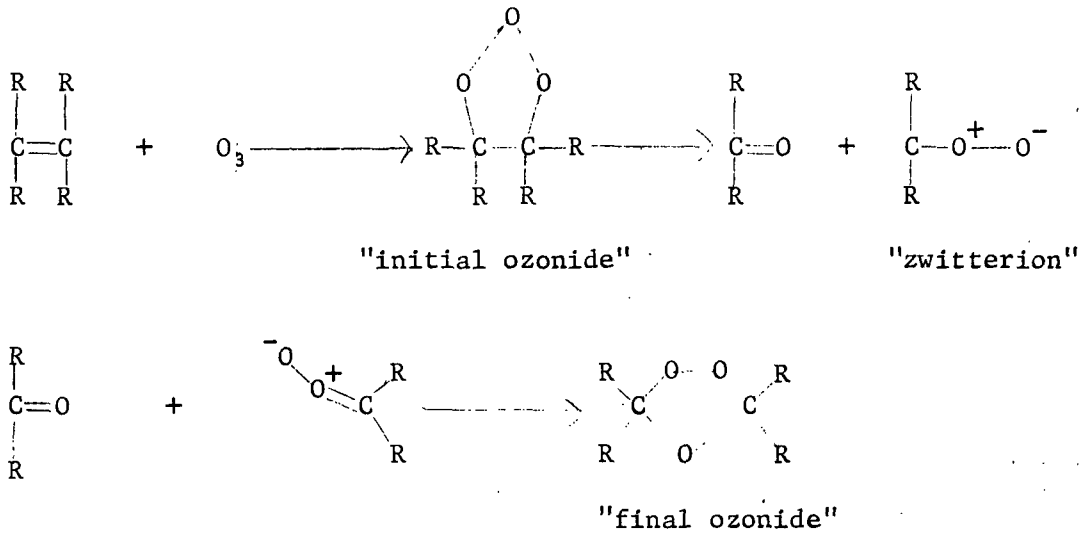

Figure 2. Criegee Mechanism for Ozonation of Olefins

The second pathway involves reaction of the zwitterion with participating solvents. Figure 3 illustrates a zwitterion reaction with water to form hydroxy-hydroperoxide, which can in turn hydrolyze to formaldehyde and hydrogen peroxide.

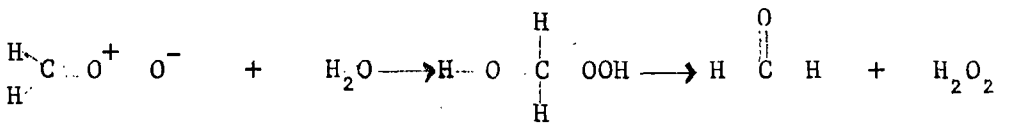

Figure 3. Reaction of Zwitterion with Water

The third route for zwitterion reaction involves dimerization. Products of this reaction are cyclic diperoxides or polymeric peroxides. A dimerization reaction is illustrated below (Fig. 4).

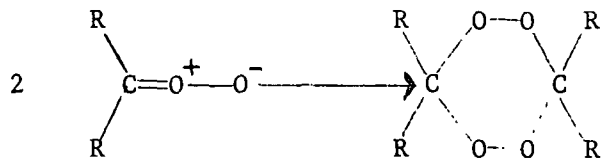

Figure 4. Dimerization of Zwitterions to Form Cyclic Diperoxide

OZONE REACTIONS WITH LIGNIN

Investigations of ozone reactions with lignin model compounds and isolated lignins have been performed by a number of researchers. Lignin substrates have ranged from monomeric and dimeric lignin model compounds to more complicated structures including HCl, methanol, kraft, and sulfite lignins.

Model Studies

A number of studies involving ozonation of lignin model compounds have been performed by various researchers (9-12). The model compounds used in all of these studies were derivatives of guaiacyl or veratryl nuclei and the ozonations were run in solution as homogeneous reactions (see Fig. 5).

Figure 5. Guaiacyl and Veratryl Nuclei

The work of Hatakeyama, et al. (9) and Kratzl, et al. (10) involved monomeric lignin models, Balousek (11) used a dimeric β-aryl ether model, while Kojima, et al. (12) worked with both monomeric and dimeric lignin models.

The important findings of the above-mentioned studies are discussed in the following paragraphs.

A selective ring-cleavage reaction was observed between the oxygen-bearing substituents of the aromatic ring upon ozone treatment (9-12). This resulted in formation of muconic acid derivatives which underwent rearrangement, and were usually isolated as muconate lactones (9,11,12). An example is shown in Fig. 6.

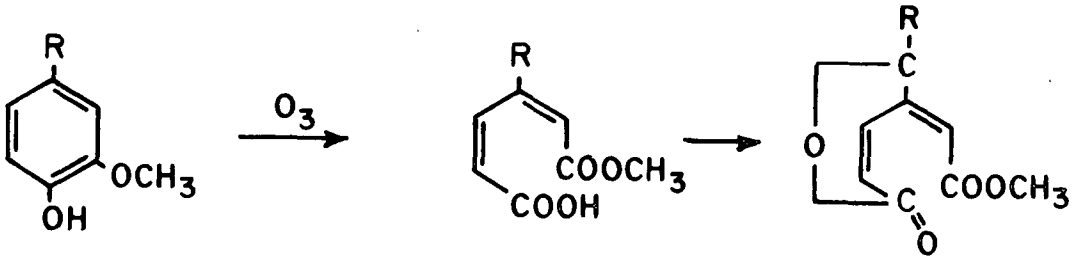

Figure 6. Selective Ring-Cleavage Reaction for Ozone-Oxidation of Lignin Model

Kojima, et al. (12) observed selective ring cleavage between carbons 3 and 4, and also found the reaction occurred preferentially at the more substituted aromatic ring for dimeric lignin models. Other ring-cleavage reactions were also observed to occur depending on model structure and specific reaction conditions (10).

Ultimate degradation of the aromatic ring in lignin models was found to produce primarily acidic reaction products (9-12) (Fig. 7).

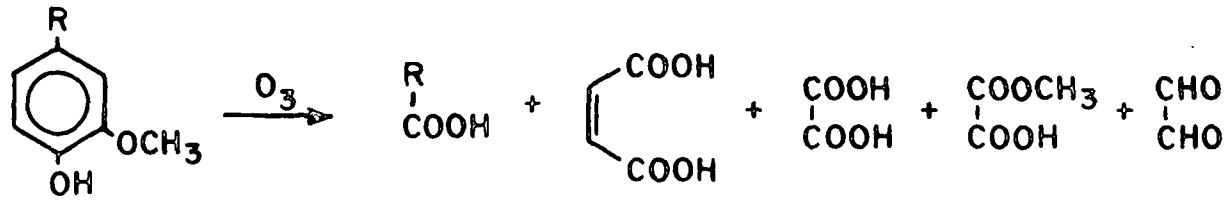

Figure 7. Ozone-Oxidation of Lignin Model to Form Acidic Reaction Products

Side-chain oxidation was also observed in the ozonation of lignin model compounds (9,12) (Fig. 8). This characteristically resulted in formation of aldehydic or carboxylic functional groups.

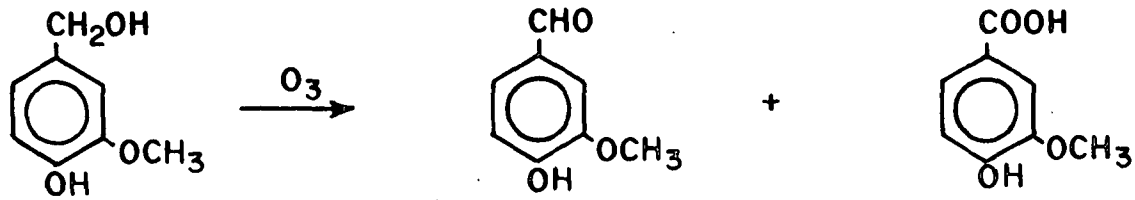

Figure 8. Ozonation of Side-Chain in Lignin Model Compound

Kojima, et al. (12) found the reactivity of lignin models with ozone was significantly affected by the α-substituent on the lignin side chain. Electron-withdrawing groups, especially carboxyl, were found to hinder oxidation of the model compounds. Kratzl, et al. (10) also found the reactivity of lignin models was strongly dependent on the nature of the substituents. Electron-withdrawing groups reduced reactivity, while electron-releasing groups increased reactivity.

Kojima, et al. (12) found the reactivity of dimeric lignin models toward ozone was noticeably affected by the type of bonding between the lignin monomer units. The reactivity of dimeric lignin models was observed to decrease in the order biphenyl > phenyl coumaran > β-aryl ether.

Balousek (11) and Kojima, et al. (12) both found ozonation of dimeric lignin models was capable of cleaving the bonds connecting the lignin monomers. This resulted in the formation of the muconate lactones and side-chain oxidation products mentioned previously (Fig. 6 and 8) as well as several other types of oxidation products (see Fig. 9-11).

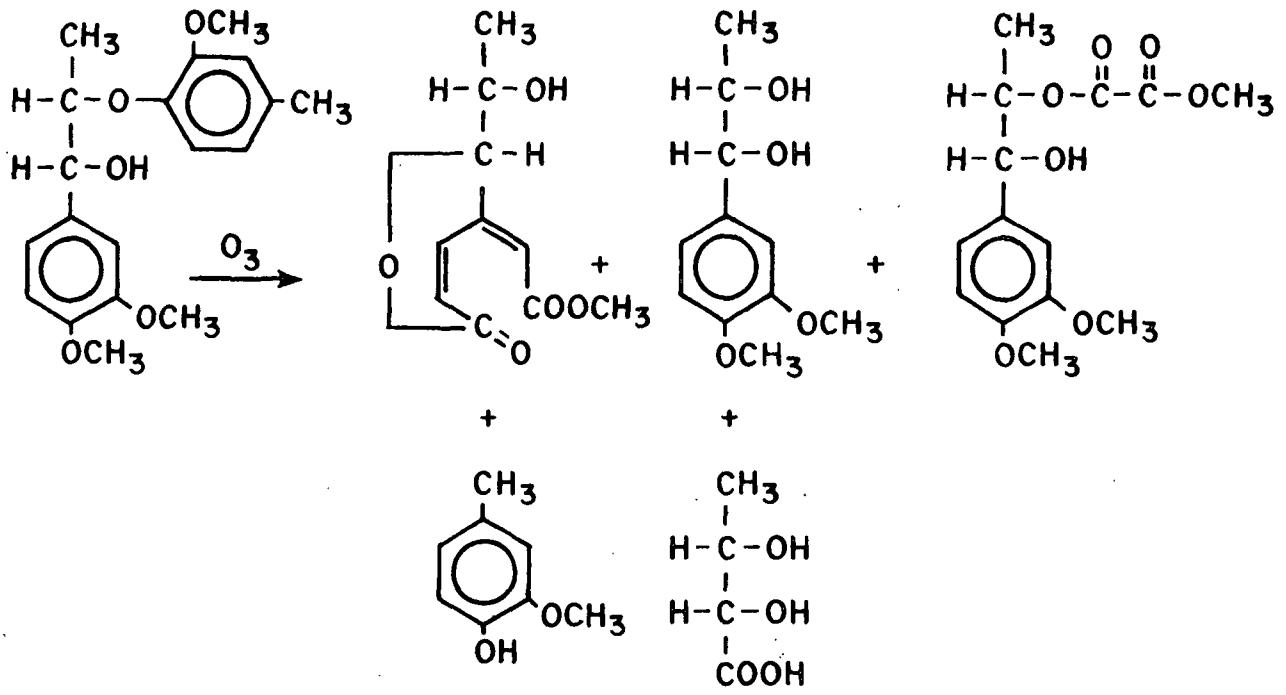

Figure 9. Ozonation of β-Aryl Ether Lignin Model According to Balousek (11)

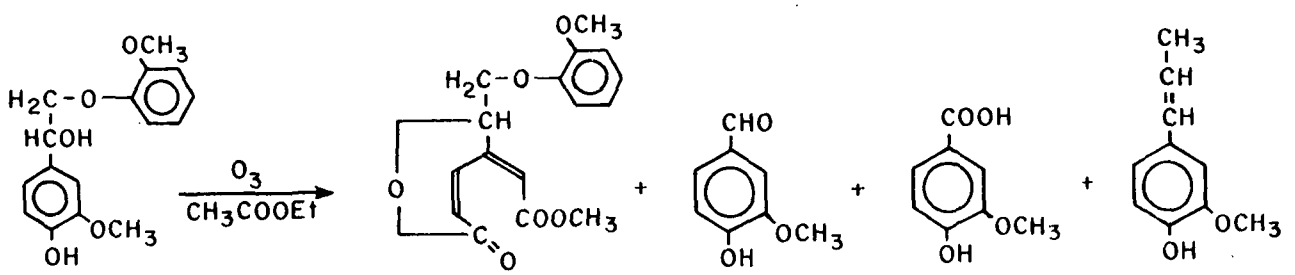

Figure 10. Ozonation of β-Aryl Ether Model According to Kojima et al. (12)

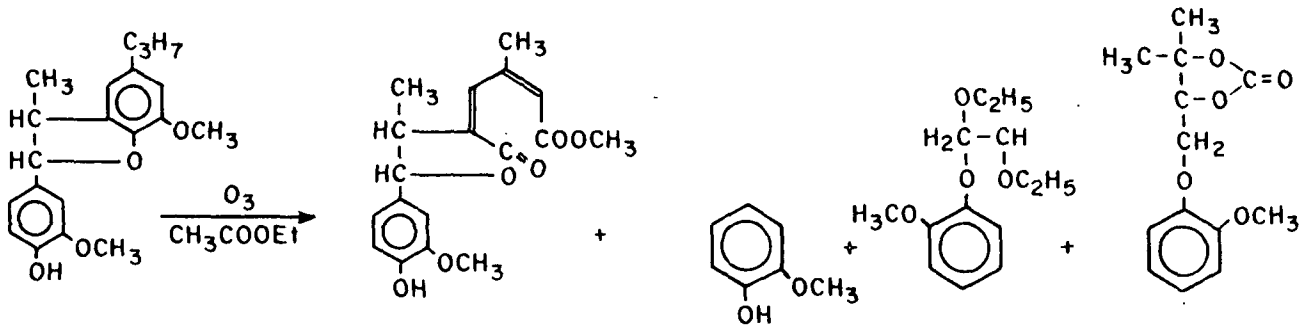

Figure 11. Ozonation of Phenyl Coumaran Lignin Model According to Kojima, et al. (12)

In addition to the aromatic ring and side-chain oxidation reactions occurring upon ozonation of lignin model compounds, Kojima, et al. (12) identified a polycondensed reaction product (Fig. 12) that suggested radical coupling reactions were also taking place.

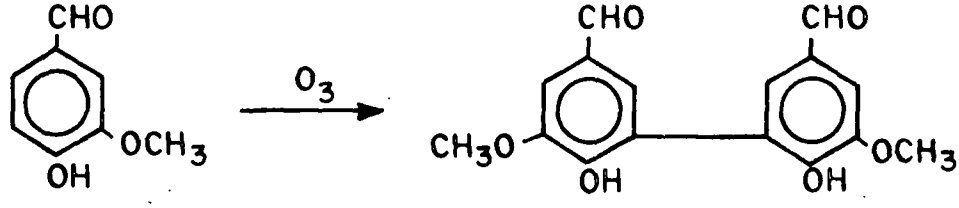

Figure 12. Formation of Polycondensed Reaction Product Through Ozonation of Lignin Model Compound (12)

Kojima, et al. (12) postulated this product arose from radical coupling of phenoxy radicals.

Kratzl, et al. (10) found active oxygen was formed upon ozonation of lignin model compounds. This indicated ozonides, hydroperoxides, peroxides, and/or quinone functionalities were produced (13).

Kratzl, et al. (10) managed to isolate crystalline ozonides by reacting lignin models at low temperature (-35°C), however, these ozonides were rather unstable and decomposed upon heating.

They also isolated ethyl formate as a reaction product. It was postulated this compound arose from rearrangement of a hydroperoxide intermediate (see Fig. 13). The hydroperoxide was probably formed by reaction of the solvent, in this case ethanol, with a zwitterion that was formed during the ozonation.

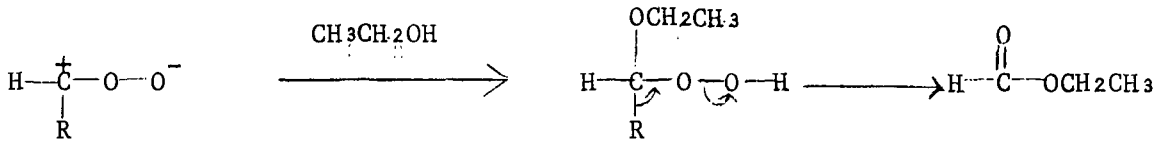

Figure 13. Formation of Hydroperoxide from Zwitterion and Rearrangement to Ethyl Formate

Summary - Ozone Reactions with Lignin Model Compounds

Ozone-oxidation of lignin model compounds involves ring opening, side-chain oxidation, and radical coupling reactions. Secondary reactions resulted in further degradation and solvent interaction with the primary products.

A large variety of reaction products are formed upon ozone degradation of the lignin models, most of which contained oxygen functionalities (carbonyl, carboxyl) introduced through ozonation.

Isolated Lignin Studies

Hatakeyama, et al. (14) ozonated calcium lignosulfonate in water. They observed an increase in the number of carboxyl groups present in the ozonated lignin, and a decrease in the number of α-carbonyl, methoxyl, and phenolic hydroxyl groups. Both maleic and oxalic acids were detected in the ether-extracted reaction solutions.

In ozone experiments with methanol lignin, Katuscak, et al. (15) observed changes in UV, IR, and NMR spectra, as well as lignin molecular weight. Interpretation of the spectra indicated an increase in carbonyl and carboxyl groups in the ozonated lignin. A destruction of the aromatic conjugated system was also noted. The number average molecular weight of the methanol lignin declined from 1700 to 550 in 1 hour.

Kratzl, et al. (10) reacted unmodified, and acetylated and methylated kraft lignin with ozone. They observed formation of acidic groups they assumed to be primarily carboxyl. Higher contents of acidic groups resulted in greater yields of water-soluble material. Insoluble lignin material was found to contain, at most, 15% carboxyl groups. Evidence for muconic acid formation via selective ring cleavage between C-3 and C-4 was also provided by their results.

In other studies with methanol and HCl lignins, Katuscak, et al. (13,16,17) found ozonation of these isolated lignins resulted in formation of stable-free radicals (based on ESR analysis). The polymeric matrix of the lignin macromolecule and the aromatic conjugated system had a stabilizing influence on the free-radicals formed by ozonation. Radical decay was promoted by ozone degradation of the aromatic conjugated system and loss of molecular weight.

Active oxygen functional groups (hydroperoxides, ozonides, peroxides) were also detected in ozonized HCl and methanol lignin (13). There formation was found capable of promoting polymerization reactions (17). It was proposed the polymerizations were initiated by lignin macroradicals and/or hydroxyl radicals formed from the hydroperoxide derivatives in the ozonized lignin.

Katuscak, et al. (17) found evidence for solvent interaction of tagged methanol ($^{14}CH_3OH$) with the zwitterions formed in ozonated lignin. They postulated the formation of the hydroperoxide intermediate shown in Fig. 14.

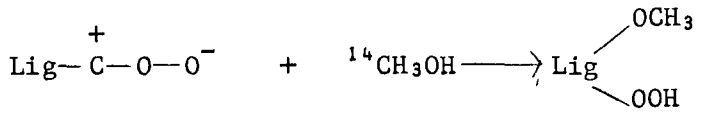

Figure 14. Reaction of Zwitterion in Ozonized Lignin with Solvent

Proposed Reaction Mechanisms for Ozone-Oxidation of Lignin

Based on model compound, isolated lignin, and mechanical pulp studies, various researchers have proposed mechanisms to explain the reaction of lignin with ozone. Both ionic and free-radical mechanisms have been proposed.

Ionic Mechanisms

Soteland (18) suggested the initial reaction of ozone with lignin involves the olefinic bonds present in coniferaldehyde and related structural units (see Fig. 15). A 1,3 dipolar addition mechanism, analagous to that proposed by Criegee (8) for ozonation of olefins, is probably also operating in lignin.

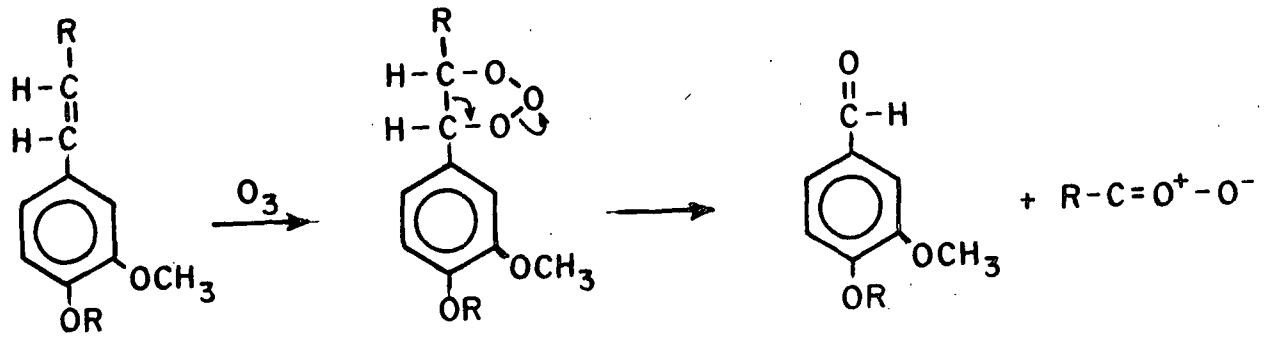

Figure 15. Reaction of Olefinic Bond in Lignin with Ozone as Proposed by Soteland (18)

The reaction results in the formation of a vanillin derivative and a zwitterion which can react as described previously in the section on olefins.

The extent of the reaction shown in Fig. 16 is rather limited since only about one in twenty lignin C-9 units possess an olefinic linkage (19,20).

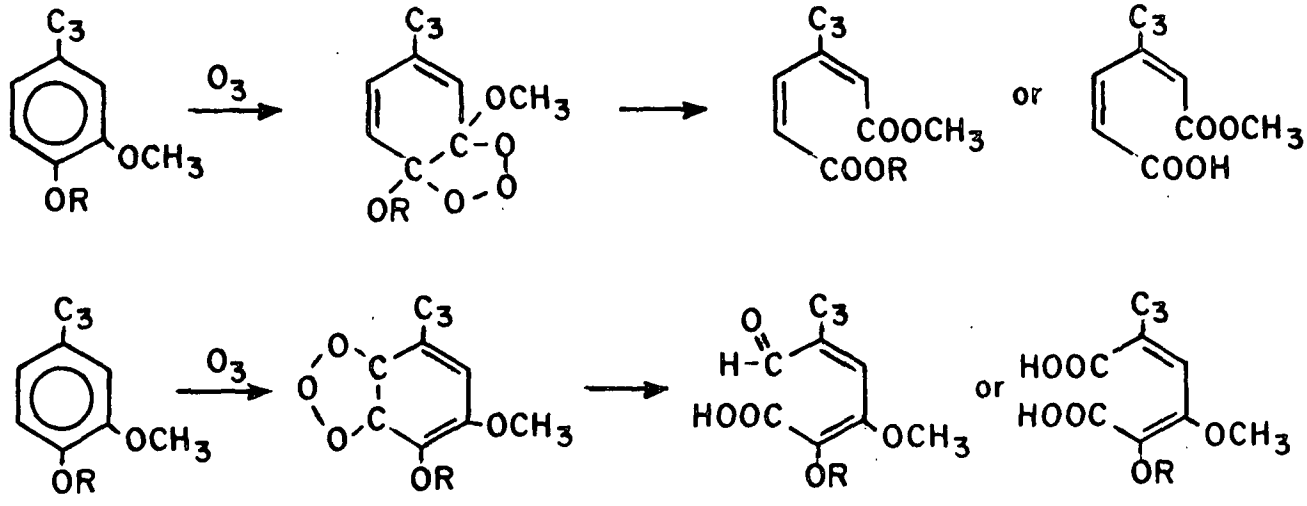

Figure 16. Reaction of Aromatic Bonds in Lignin via 1,3 Dipolar Addition of Ozone

Structural units with the next reactivity toward ozone were postulated to be the aromatic rings present in lignin (18). The aromatic bonds provide sites for both 1,3 dipolar addition and electrophilic substitution reactions (6).

With limited amounts of ozone, addition reactions result in ring cleavage to form muconic acid derivatives. Attack between carbons 3 and 4 is probably favored (based on the results of model studies), but the other aromatic bonds are also involved. Reaction mechanisms similar to those proposed by Soteland (18) and Singh (6) are shown in Fig. 16.

Aromatic ring cleavage reaction such as those shown in Fig. 17 result in exposure of what are now olefinic bonds. These bonds are very labile to further attack by excess ozone. Soteland (18) proposed a mechanism for degradation of muconic acid derivatives that is shown in Fig. 17.

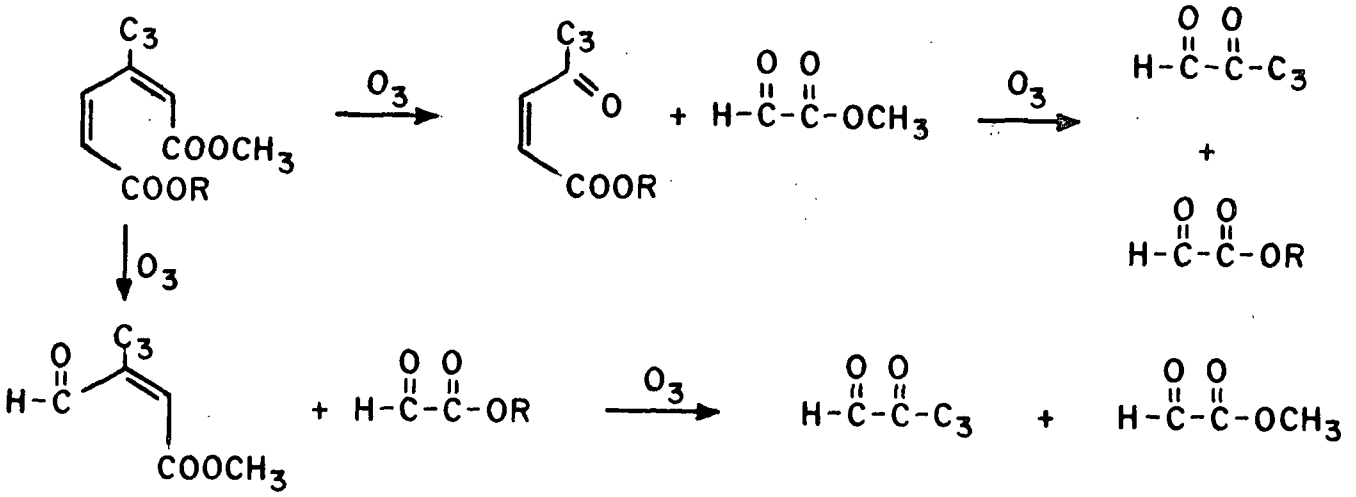

Figure 17. Ozone Degradation of Muconic Acid Derivatives in Lignin as Proposed by Soteland (18)

Ozone attack of muconic acid structures was postulated to produce a complex mixture consisting of glyoxal and glyoxylic acid derivatives (18).

A second possible mechanism of ozone attack on lignin aromatics is via aromatic electrophilic substitution reactions. These reactions do not involve initial ring cleavage, but rather ring hydroxylation or demethoxylation (6). Plausible electrophilic substitution mechanisms based on the lignin model studies of Hatakeyama, et al. (9) and the interpretation of Singh (6) are given in Fig. 18.

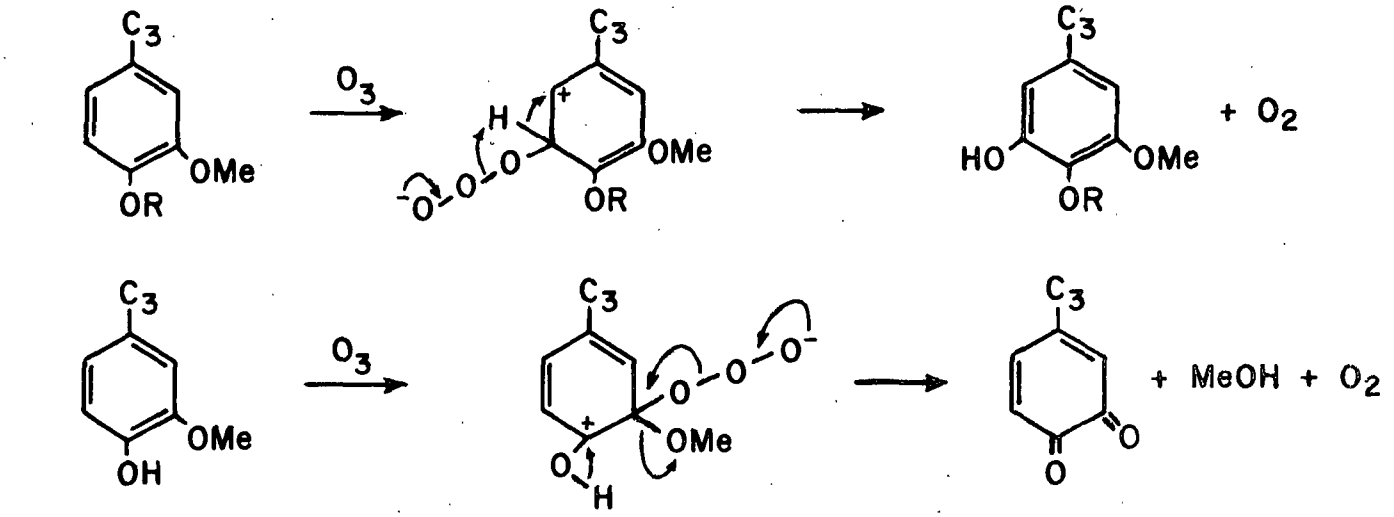

Figure 18. Reaction of Lignin with Ozone via Aromatic Electrophilic Substitution Mechanism Proposed by Singh (6)

Attack of ozone at the carbon-hydrogen bonds of the lignin side chain was also postulated to occur (6). Ozone attack at carbon-hydrogen bonds has been demonstrated to occur readily for aldehydes, ethers, and alcohols (21,22). An ozone insertion mechanism was proposed responsible for oxidation of the side chains in lignin (6). The ozone insertion mechanism, as applied to lignin side chains, is illustrated in Fig. 19.

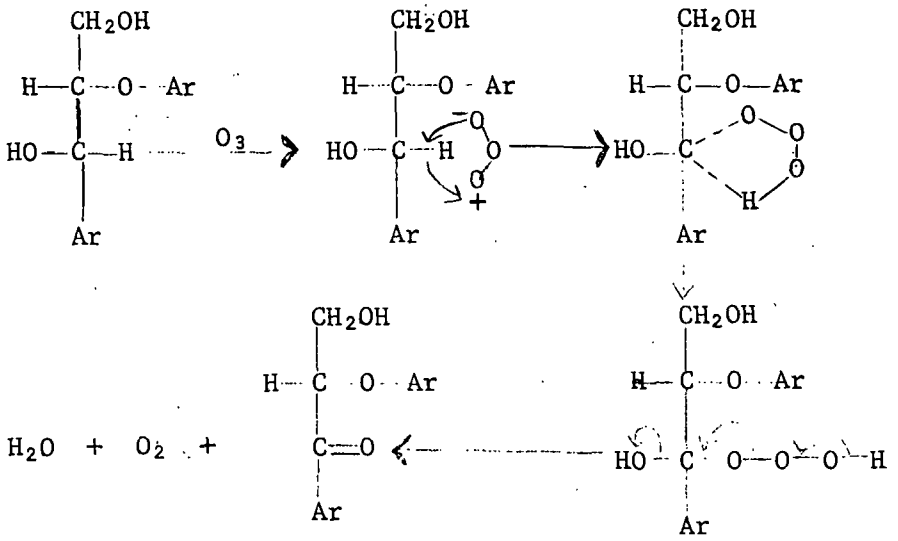

Figure 19. Oxidation of Lignin Side-Chain via Ozone Insertion Mechanism

It should be mentioned that ozone attack at the carbon-hydrogen bonds opposite the β-aryl ether linkage in lignin provides a route for cleavage of the ether bonds.

Free-Radical Mechanisms

The formation of stable free-radicals upon ozonation of lignin has been demonstrated by Katuscak, et al. (13,16,17). He proposed the initiation reaction shown in Fig. 20 for generation of free-radicals in lignin.

Figure 20. Ozone Initiation Reaction for Generation of Free-Radicals in Lignin

Hoigne and Bader (23) found that hydroxyl radicals were the main oxidants formed in the decomposition of ozone in water (Fig. 21). The reaction was catalyzed by hydroxide ions or other radicals. Thus a second route for generation of free-radicals in aqueous lignin systems was afforded based on their results.

$$H_2O + O_3 \xrightarrow{\cdot R \text{ or } OH^-} 2\,(\cdot OH) + O_2$$

Figure 21. Decomposition of Ozone in Water to Form Hydroxyl Radical (23)

Once free-radicals are generated in the lignin system, many propagation and termination reactions are possible. Some of the plausible reactions are shown in Fig. 22 and 23.

$$\text{Lig—O}\cdot + \text{Lig—H} \longrightarrow \text{Lig}\cdot + \text{Lig—OH}$$

$$\text{Lig}\cdot + O_2 \longrightarrow \text{Lig—O—O}\cdot$$

$$\text{Lig—O—O}\cdot + \text{Lig—H} \longrightarrow \text{Lig}\cdot + \text{Lig—OOH}$$

$$\text{Lig—H} + \cdot OH \longrightarrow \text{Lig}\cdot + HOH$$

$$\text{Lig—H} + \cdot OOH \longrightarrow \text{Lig}\cdot + H_2O_2$$

Figure 22. Free-Radical Propagation Reactions in Lignin

$$\text{Lig}\cdot + \text{Lig} \longrightarrow \text{Lig—Lig}$$

$$\text{Lig}\cdot + \cdot OOH \longrightarrow \text{Lig—OOH}$$

$$\text{Lig}\cdot + \cdot OH \longrightarrow \text{Lig—OH}$$

$$\text{Lig—O}\cdot + \text{Lig}\cdot \longrightarrow \text{Lig—O—Lig}$$

$$\text{Lig—O}\cdot + \cdot OH \longrightarrow \text{Lig—OOH}$$

$$HO\cdot + \cdot OH \longrightarrow H_2O_2$$

Figure 23. Free-Radical Termination Reactions in Lignin

It should be noted that free-radical reactions can account for production of lignin condensation products, hydroperoxide functionalities, and hydrogen peroxide.

Secondary reactions, such as decomposition of hydroperoxides, result in further oxidation of the lignin, ultimately forming carbonyl and carboxyl groups (17).

Summary of Ozone Reactions with Lignin

Ozone reacts initially and most rapidly with olefin groups present in lignin and then with the aromatic nuclei. In the absence or inaccessibility of these structures, ozone will also react with many different carbon-hydrogen bonds typical of those found on the lignin side chains.

Ozonation of aromatic rings in lignin involves both 1,3 dipolar addition and electrophilic substitution reaction mechanisms. Addition reactions result in ring-opening and formation of muconic acid derivatives, which are very labile to further ozone-oxidation due to the presence of olefinic bonds. Electrophilic substitution hydroxylates the ring, or results in demethoxylation and subsequent quinone formation. Molecular oxygen is liberated in both cases.

An ozone insertion mechanism appears plausible in lignin side-chain oxidation. Carbonyl functionalities are introduced into the chain and cleavage of the α- or β-aryl ether linkage is conceivable.

The reaction of ozone with lignin also involves the formation of free-radicals, including hydroxyl, perhydroxyl, and various lignin macroradicals. The free-radicals initiate lignin condensation reactions and result in the

formation of hydroperoxide functionalities in lignin. Decomposition of the hydroperoxides leads to further lignin oxidation and formation of carbonyl and carboxyl groups.

OZONE REACTIONS WITH CELLULOSE

Since the substrate in this study was wood rather than an isolated lignin, possible reaction of ozone with the holocellulose component of the wood must also be considered.

Katai and Schuerch (24) performed a study involving ozonation of α-methyl glucoside, methyl cellulose, and an unbleached kraft pulp. They found ozonation resulted in formation of glucose as a primary reaction product from methyl glucoside and observed a large drop in degree of polymerization for ozonized methyl cellulose and kraft pulp.

The reaction solutions for methyl glucoside and methyl cellulose were strongly acidic (pH = 2.2-2.7) and contained methanol, formaldehyde, and formic acid as volatile materials. Traces of what were believed to be mixed muconic acids and lactones were also found.

Based on the results of their study, Katai and Schuerch (24) postulated direct ozone attack (ozone-initiated hydrolysis) was the most important reaction mechanism with regard to ozonation of cellulosic materials. The proposed mechanism is shown in Fig. 24.

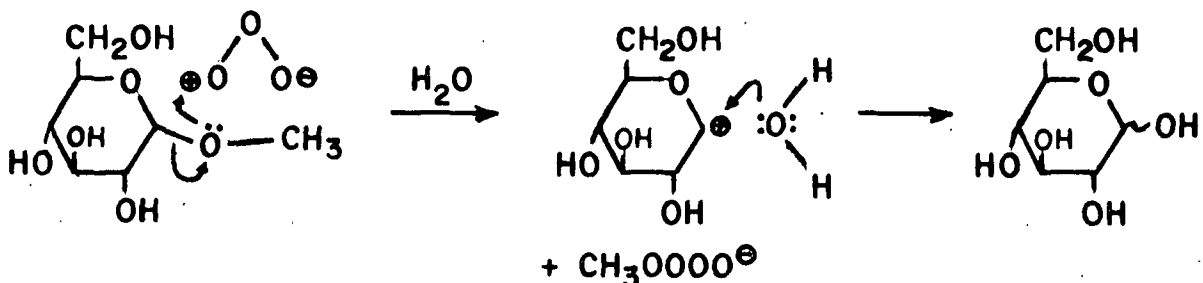

Figure 24. Mechanism for Ozone-initiated Hydrolysis of Glycosidic Linkage

Katai and Schuerch (24) also concluded ozonation of cellulosic substrates initiates an autoxidation process which leads to the formation of oxidized functional groups such as carbonyls, carboxyls, lactones, and hydroperoxides.

TREATMENT OF WOOD PULPS WITH OZONE

Numerous studies have been performed involving treatment of chemical and mechanical pulps with ozone. Ozonation of chemical pulps as a method of pulp bleaching has been studied at various reaction conditions for kraft (4,25,26), sulfite (4), and oxygen/alkali pulps (27).

Ozonation of mechanical pulps has been studied primarily as a process to enhance strength properties of groundwood, refiner, and thermomechanical pulps. Brightness increase is generally of secondary importance.

Typical reaction conditions for ozone treatment of wood pulp are pulp consistency of 40%, ozone charge of 0.2-2.0% (on o.d. wood), temperature of 0-45°C, and time of 5-30 min.

The ozone reaction with wood pulps is very sensitive to pulp moisture content with optimum reaction occurring at 40% consistency (25). Schuerch (26) postulated the water layer surrounding the pulp fibers is the rate controlling factor. At very low moisture content the fibers are effectively impervious to ozone attack except for superficial surface oxidation. At very high water contents the rate of ozone-fiber reaction is decreased by the slow rate of ozone diffusion through the liquid layer.

OZONE BLEACHING OF CHEMICAL PULPS

Ozone has been shown to be an effective bleaching agent for chemical pulps only when combined in a multistage bleaching process where ozone treatment is

followed by additional pulp treatment with hypochlorite, peroxide, or chlorine dioxide (27). A fully-bleached (brightness 92.4%) kraft eucalyptus pulp was obtained by Soteland (4) using a two-stage ozone treatment (1 + 1% O_3) followed by 2% active chlorine treatment in the form of hypochlorite. Singh and Secrist (25) were able to produce a fully-bleached (brightness 90%) kraft hardwood pulp using an O_3 + DED sequence.

Rothenburg, et al. (27) were able to bleach oxygen pulps to a brightness of about 80% using an O_3EO_3 sequence, but similar bleaching experiments performed with kraft pulps yielded slightly lower (2-8%) brightness values.

An inherent problem associated with ozone bleaching is the indiscriminant manner in which ozone attacks both lignin and carbohydrate material. This results in ozone-bleached pulps having a substantially lower viscosity than pulps bleached by conventional means.

Singh and Secrist (25) found kraft pulps bleached to a brightness of 90 had viscosities of 19 and 10 cp for CEDED and O_3DED sequences, respectively. However, it has been shown the large viscosity drops observed for ozone-bleached pulps do not result in substantial changes in the mechanical strength properties of the pulps. Ozone-bleached pulps tend to have lower (on the order of 10%) tearing and folding endurance than pulps bleached by traditional methods, but other strength properties are approximately equal. There is no indication of fiber strength loss (25,28).

Ozone-bleached pulps tend to beat significantly faster than conventionally bleached pulps and have a high sheet-bonding capacity. This is attributed to fiber surface modification during the bleaching process which promotes increased fiber swelling and fibrillation. Ozone-bleached pulps also display significantly improved stability toward flourescent light (25,27).

EFFECT OF OZONE ON MECHANICAL PULPS

Soteland (1,2,18) found limited ozone treatment (5% or less on o.d. pulp basis) of mechanical pulps resulted in significant strength improvement without excessive yield loss. The strength enhancement was attributed to increased hydrophilicity and swelling properties of the lignin-containing fibers (2).

Ozonation of mechanical pulps resulted in the formation of carboxyl and carbonyl groups in the pulp, and a corresponding decrease in the aromatic character of the lignin (1-3). A correlation between pulp carboxyl content and breaking length was found (3).

Soteland (1) observed a brightness reduction of 2-4 units for softwood mechanical pulps treated with ozone, while ozonated hardwood pulps showed a considerable brightness increase. Lindholm (29) found ozone treatment of mechanical pulps had a negative effect on pulp optical properties, including brightness.

Soteland (1) recovered the water-soluble material from a spruce groundwood pulp treated with 3% ozone and then water washed. The isolated material consisted of 75% lignin degradation products plus oxidized extractives, while the remaining material was of carbohydrate composition.

In a separate study Soteland (18) ozonized a western hemlock groundwood pulp and isolated the acetone-water-soluble degradation products. The isolated material was acidic and the presence of active oxygen and oxalic acid was demonstrated.

Infrared spectra of the ozonized lignin fractions showed the aromatic character of the lignin had almost completely disappeared and extensive formation

of carbonyl groups was evident. Carbonyl groups were attributed to carboxylic acid formation. Soteland (18) also found evidence of methyl ester groups believed to be formed by the oxidative cleavage of methoxyl-substituted benzene rings.

EFFECT OF OZONE ON WOOD

Several studies (26,30,31) have been performed involving treatment of wood with ozone. The results indicated it was possible to pulp wood in the form of meal, shavings, chips, or blocks at room temperature with ozone. The most rapid and homogeneous pulping occurred for reactions carried out in the gas phase using fluctuating pressure and wood with a consistency of 50%. In general, the reaction of ozone with wood was found to be topochemically heterogeneous and limited largely to the surface. The extent of the reaction was greatly affected by the permeability of the wood structure.

Ozone was found to react as a rather indiscriminate reagent with any of the wood constituents. The carbohydrate fractions of the wood were degraded along with the lignin. However, the ozone appeared to attack only the amorphous regions of the cellulose, leaving the cellulose crystallites intact. A leveling off degree of polymerization (DP) of approximately 400 was observed for ozone-treated Norway spruce and basswood (30).

In ozone pulping studies by Moore, et al. (31) using red maplewood, pulping reactions appeared to be of three general types:

1. Ozonolysis of aromatic and unsaturated structures mainly by Criegee's mechanism.
2. Ozone-initiated chain oxidation of saturated functional groups leading to a variety of oxidized carbohydrate residues.

3. The hydrolysis of glycosidic linkages, with both ozone and proton participating as electrophilic catalysts.

Some degree of preferential lignin attack was also noticeable as lignin was virtually eliminated from the fiber. Glucose appeared to be the most ozone-resistant sugar as glucose percentages in the ozone pulped wood approximated those in corresponding untreated holocellulose.

OZONE PRETREATMENT OF ALKALI-FIBERIZED WOOD TO PROMOTE REACTION WITH OXYGEN-ALKALI

Johnson and McKelvey (5) have done pioneering research in the field of lignin activation with ozone. Their objective was to chemically modify the lignin present in alkali-fiberized wood thereby making it more reactive when subjected to oxygen/alkali pulping.

The ozone modification was intended to generate functional groups in the lignin which are postulated reaction sites in oxygen/alkali delignification. The two functional groups of major interest were the phenolic hydroxyl and α-carbonyl group.

Kratzl, et al. (32,33) have developed a plausible theory concerning lignin oxidation in oxygen/alkali. The theory is based upon model compound studies and suggests the importance of free-phenolic hydroxyl groups in relation to oxygen/alkali (O/A) lignin oxidation.

The α-carbonyl groups present on the lignin side chains are also postulated reaction sites in oxygen/alkali delignification, based on the lignin model studies of Aoyagi, et al. (34).

Johnson and McKelvey (5) hypothesized ozonation of fiberized wood could generate phenolic hydroxyl and α-carbonyl groups in the lignin. Thus, assuming these groups were generated in the lignin, ozone pretreated fiberized wood should show an increased susceptibility to oxygen/alkali delignification as compared to untreated wood.

Their results for ozone pretreatment of alkali-fiberized red maple indicated activation of the lignin was possible. The subsequent oxygen/alkali delignification became more selective with less carbohydrate degradation and chain degradation.

Ozone pretreatment results for alkali-fiberized loblolly pine were not as impressive. In some cases a gain in selectivity of lignin removal was observed for subsequent oxygen/alkali delignification, but the polysaccharide chains were severely degraded by O/A and the ozone pretreatment did not inhibit this degradation.

Since the phenolic hydroxyl and α-carbonyl contents were not determined for the untreated and ozone pretreated woods, it was not possible to attribute the observed increases in selectivity of lignin removal to ozone generation of these functionalities.

THESIS OBJECTIVE

The objective of this thesis was to elucidate the manner in which alkali-fiberized wood is modified by ozone treatment and to aid in determining ozone's potential use in pulping and bleaching processes.

It is hypothesized that ozone treatment of alkali-fiberized wood results in modification of the wood components. However, the extent or exact nature of this modification is not clear. This study is designed to provide a deeper insight into ozone chemistry involving lignin and wood, concentrating on ozone reactions with lignin, but also providing information concerning carbohydrates and wood in general.

EXPERIMENTAL APPROACH

The experimental approach involved treatment of alkali-fiberized wood with 1-7% ozone followed by chemical characterization of the unreacted and ozonated wood using analytical and spectroscopic techniques.

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Chemical characterization of the fiberized wood relied heavily on the use of Fourier transform infrared spectroscopy (FT-IR). The advantages of FT-IR as compared to conventional infrared spectroscopy are discussed in Appendix I.

The use of infrared spectroscopy in studies of lignin and wood are numerous (19,35-44). Band assignments pertinent to this study are shown in Appendix II.

DIFFERENCE SPECTROSCOPY

An important new technique developed for the infrared analysis of lignin and wood is difference spectroscopy (35-37). Vander Linden (36) used this technique to compare untreated spruce groundwood with chlorine-dioxide modified wood. He also estimated carboxyl contents of the untreated and modified woods by obtaining difference spectra of neutralized and unneutralized wood samples.

There is a serious drawback to the use of IR difference spectroscopy with conventional spectrometers. It is very difficult to produce two samples (usually powdered wood or lignin in KCl pellet form) for IR analysis that will have the same intensity of absorbance. Thus a certain amount of error is inherent in difference spectra obtained on conventional spectrometers where one pellet is placed in the sample beam and the other in the reference beam.

This problem of intensity variation was largely circumvented in this study through the use of the FT-IR system to obtain difference spectra. With this advanced analysis system, it was possible to balance spectra of interest against each other and correct for intensity variations, before subtraction to obtain the difference spectrum. This provided for more accurate difference spectra than could have been obtained using a conventional infrared system. It also drastically reduced the time required to obtain accurate difference spectra, thus allowing for a more comprehensive study based on this technique. Details of the balancing technique used in FT-IR difference spectroscopy are covered in the Experimental section.

With regard to functional group analysis, based on FT-IR difference spectroscopy measurements, it was necessary to assume structural changes induced through ozonation would not significantly affect the wavelength of absorption or the extinction coefficients. Further consideration of this assumption appears in appropriate sections of this thesis.

RESULTS AND DISCUSSION

OZONE OXIDATION OF FIBERIZED WOOD — TECHNICAL ASPECTS

STARTING MATERIAL

A sodium carbonate-bicarbonate fiberized loblolly pinewood (Pinus taeda) served as the starting material in this study. The alkali-fiberized wood resembled a coarse thermomechanical pulp after the first stage of refining. It was very similar to fiberized woods used in previous oxygen/alkali pulping work of Johnson and McKelvey (5).

Prior to characterization and ozonation, the fiberized wood (FW) extractives were removed by acetone extraction. Extractives are known to react preferentially with ozone (1) and this effect was therefore eliminated in this study. The pH of the extracted FW was then adjusted to near neutrality by soaking in dilute hydrochloric acid and followed by hot-water extraction (see Experimental section).

OZONE CONSUMPTION IN REACTIONS WITH FIBERIZED WOOD

Alkali-fiberized wood was treated with ozone in four separate reactions using a reactor (see Experimental section) in which the gas flowed through the FW. The flow rate of ozone to the FW was held constant and the reaction times varied to provide ozonated wood samples which had consumed 1, 3, 5, and 7% ozone on an oven-dry, fiberized wood basis.

The reaction time, ozone consumption, and ozone consumption efficiency for ozonation of alkali-fiberized loblolly pine are shown in Table I.

TABLE I

GAS-PHASE OZONATION OF ALKALI-FIBERIZED LOBLOLLY PINE

(10°C, 45-46% consistency, initial pH = 6.6)

Time, min	Ozone Consumed %[a]	Ozone Consumed/ Ozone Applied %
3.72	1.0	99.4
11.00	3.0	97.2
18.58	5.0	96.6
25.50	7.0	93.7

[a]Percent based on o.d. fiberized wood

The efficiency of ozone consumption (at constant ozone flow rate), represented by the ratio of ozone consumed/ozone applied, indicated the ozone applied to FW was rapidly and almost completely (93.7-99.4%) consumed by the wood. However, as reaction times were lengthened, and therefore application levels increased, a decreasing trend in the efficiency of ozone consumption was observed.

Figure 25 illustrates this trend and suggests a linear relationship exists between efficiency of ozone consumption and the amount of ozone consumed by FW. Regression analysis was used to obtain the line and correlation coefficient in this and all following figures.

A similar decrease in efficiency of ozone consumption was observed by Whitsitt, et al. (44) for recycled wood fibers treated with ozone.

The efficiency results suggested available reaction sites on the fiber surface were decreasing with increasing ozone consumption. Electron micrographs of ozonated fibers from recycled (44) and groundwood (45) pulps have

shown ozone reacts primarily with the fiber surface. Thus as greater amounts of ozone were applied to the fiberized wood, more of the surface reactive sites were utilized, and on continued application of ozone, the efficiency of ozone consumption decreased accordingly.

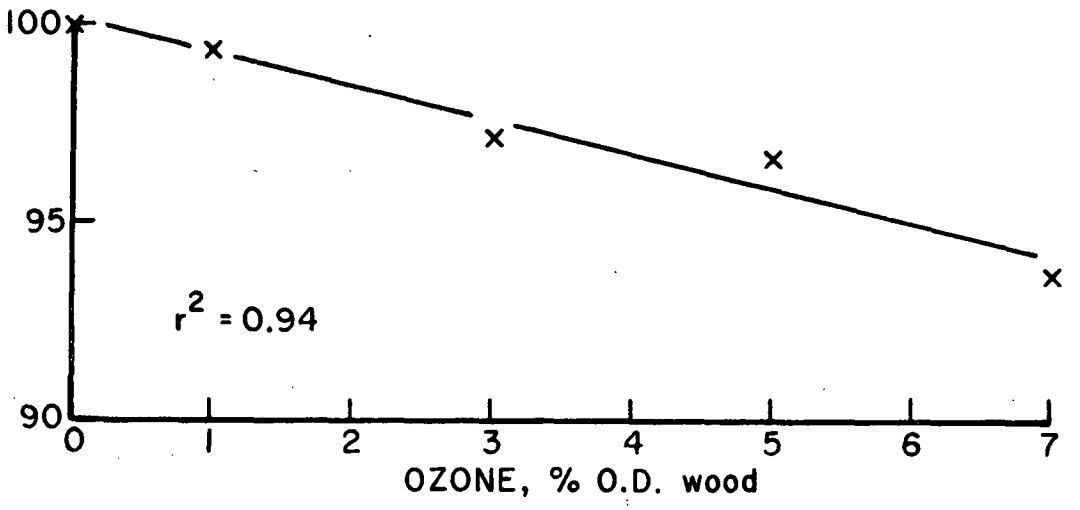

Figure 25. Efficiency of Ozone Consumption in Reactions With Fiberized Wood

Another explanation of the decreasing efficiency was afforded through the "balling" phenomena that was observed to occur as the FW tumbled about inside the reactor. The formation of small balls of fiberized wood, and thus an increase in void volume in the reactor (at the longer reaction times), may have resulted in less effective diffusion of ozone to the fiber surface, and a corresponding decrease in efficiency of consumption.

EFFECT OF OZONATION ON FIBERIZED WOOD YIELD

The unwashed and water-washed yields were determined for the ozone-treated FW. The results are given in Table II.

TABLE II

UNWASHED AND WASHED YIELD FOR OZONATED FIBERIZED WOOD YIELD

(% o.d. fiberized wood)

This Work		Literature[a]
Unwashed	Washed	Washed
102.1	98.8	96
104.0	93.3	93
103.5	90.8	90
103.6	85.7	-

[a] Work of Soteland (1) for thermomechanical pulp from pine

The ozonation of fiberized wood resulted in an initial increase in yield for unwashed wood. This verified that consumption of ozone by the FW had occurred.

The yield losses found for washed, ozonized FW indicate ozonation resulted in solubilization of wood components. Higher levels of ozonation caused greater wood solubilization. An acid-wash experiment (see Experimental section) showed more than an acid-wash treatment of FW was required to solubilize wood components to the extent observed in ozonation. Thus, ozone oxidation of FW must be chemically modifying the lignin and/or carbohydrate fractions of the wood to effect their solubilization.

The washed yields found for ozonated fiberized wood (Table II) compared favorably with those obtained by Soteland (1) for an ozonized thermomechanical pine pulp. Soteland (1) had attributed the high yield losses at relatively low ozone consumption levels, in part, to the dissolution of oxidized extractives. Since the fiberized wood used in this study was extractive-free, ozone-oxidation of extractives could not have contributed to yield loss.

From a technical standpoint, if high yield losses are to be avoided (i.e., use of ozone as a lignin modification agent) ozone consumption must be kept low.

Figure 26 illustrates the washed yields at each level of ozone consumption. It appears there is a linear relationship between washed yield and ozone consumption.

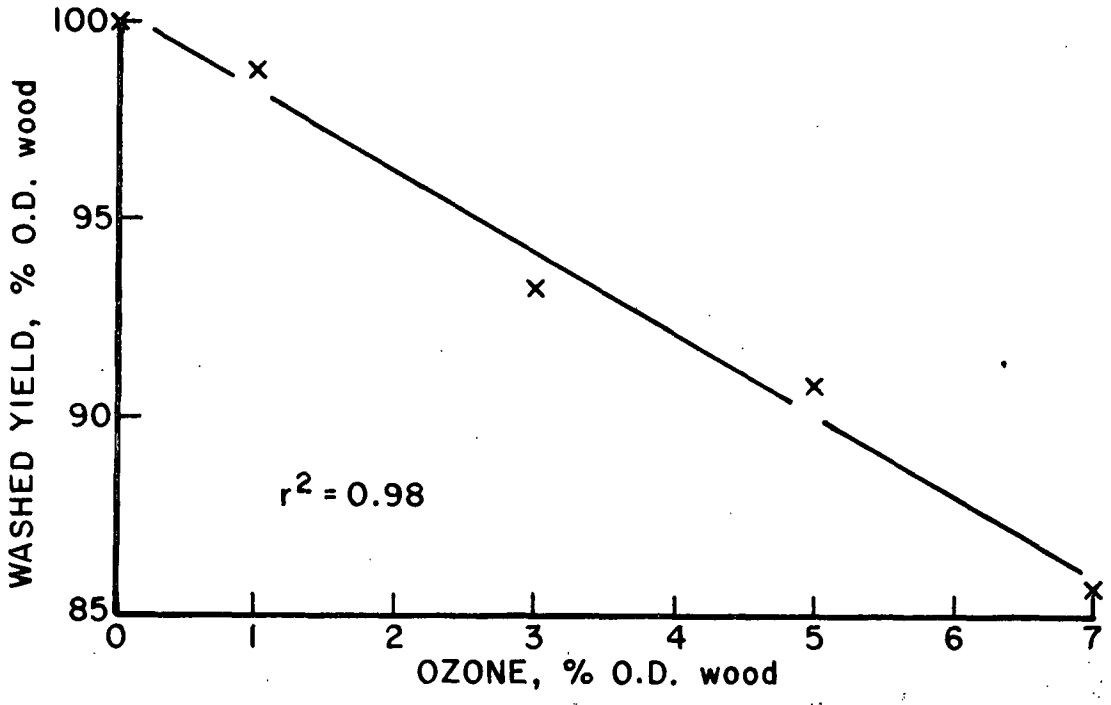

Figure 26. Washed Yield Versus Ozone Consumption for Alkali-Fiberized Wood

DELIGNIFICATION OF FIBERIZED WOOD WITH OZONE

The lignin contents of untreated and ozonated FW were determined. The amount of lignin solubilized by ozone treatment was then calculated, at each ozonation level, based on the total lignin contents (acid-soluble + Klason). The results are given in Table III.

TABLE III

LIGNIN CONTENT AND SOLUBILIZED LIGNIN FOR UNTREATED AND OZONATED FIBERIZED WOOD

Ozone, %	Lignin Content (% o.d. wood) Klason	Acid-Soluble	Total	Solubilized Lignin, %[a]
0.0	27.7	.4	28.1	-
1.0	26.1	.5	26.6	5
3.0	22.3	.5	22.8	19
5.0	19.4	.5	19.9	29
7.0	16.4	.8	17.2	39

[a]Percent based on original lignin content of untreated fiberized wood

The total lignin content of 28.1% found for untreated FW compares favorably with values of 28.3% and 28.5% obtained by Lewis (46) and Leopold (47), respectively, for loblolly pinewood.

The small acid-soluble lignin content found for untreated FW is characteristic of softwood lignin (48,49). Ozonation of FW increased the acid-soluble lignin contents slightly. Oxidative treatment of wood materials, especially with acid chlorite, has been shown to increase the acid-soluble lignin content (48).

Ozone oxidation of fiberized wood was already found capable of increasing the wood's water solubility through chemical modification of the wood components (i.e., yield's less than 100%). Therefore, it is not surprising the acid solubility of the FW lignin was also increased by ozone treatment.

The total lignin contents (Table II) obtained for ozonated FW were less than the total lignin content found for untreated FW. The lignin contents were

also observed to decrease as ozone consumption levels were increased. Values calculated for solubilized lignin (Table II) indicated 5-39% of the lignin originally present in untreated FW was solubilized by ozone treatment. Thus, ozone oxidation of fiberized wood resulted in delignification of the wood, with the extent of delignification depending on the severity of the ozone treatment.

The significant delignification obtainable upon ozonation of FW suggests the possible use of ozone as a pulping agent for fiberized wood. A two-stage process might prove more advantageous, with ozone used in the first stage for bulk lignin removal, and another chemical pulping agent used to complete the delignification.

Aromatic Content of Fiberized Wood Lignin

The aromatic content of untreated and ozonated FW was compared using FT-IR difference spectroscopy. Infrared absorbance at 1600 and 1505-1515 cm^{-1} in FW represents the carbon-carbon bond stretching mode of the aromatic rings in lignin (19,35,37-43).

Normalized absorbance values (see Experimental section for details of normalizing process) were obtained at a wavelength of 1510 cm^{-1} for untreated and ozonated, washed FW samples. At this wavelength holocellulose is essentially transparent to infrared radiation (35). The normalized absorbance values were then used in conjunction with the lignin contents of each FW sample to calculate aromatic absorptivities. The results are shown in Table IV.

TABLE IV

AROMATIC ABSORBANCE AND ABSORPTIVITY
FOR UNTREATED AND OZONATED FW

Ozone, %	Normalized[a] Absorbance	Lignin, mg[b]	Absorptivity, Absorbance/mg lignin
0.0	0.227	0.281	0.808
1.0	0.198	0.269	0.736
3.0	0.174	0.244	0.713
5.0	0.154	0.219	0.703
7.0	0.129	0.201	0.642

[a]Infrared absorbance at 1510 cm^{-1} for neutralized FW samples.

[b]Based on 1-mg sample o.d. fiberized wood.

The decrease in absorbance (at 1510 cm^{-1}) for ozonated FW shows ozone treatment resulted in degradation of aromatic rings in FW lignin. Higher levels of ozonation caused greater reductions in aromaticity. The absorbance decrease parallels the decrease in lignin content found for ozonated FW. Similar trends of decreasing aromatic absorption (1600, 1505-1515 cm^{-1}) were observed for all infrared spectra obtained from ozonated FW samples (see Appendices IV-VIII). Soteland (18) also observed decreasing aromatic absorbance at 1600 and 1512 cm^{-1} for ozonated western hemlock groundwood.

The absorptivities shown in Table IV represent the ratio of aromatic rings to lignin in fiberized wood. Since they decreased as ozone levels increased, it was concluded there were fewer aromatic rings, per equivalent amount of lignin, in ozonated FW than untreated FW. Based on absorptivity, it was estimated about 20% of the aromatic rings in 7% ozonized FW were oxidized to some extent.

If the aromatic rings are modified by ozone treatment (i.e., ring cleavage to nonaromatic structures), but not solubilized by water washing, the IR absorbance at 1510 cm^{-1} is still lost since the modified ring is no longer in aromatic form. Assuming chemical lignin analysis (Klason + acid-soluble) still measures the modified ring as lignin, a decrease in absorptivity is observed. However, if the ozone-modified ring structure is solubilized by water washing, a drop in both IR absorbance and lignin content occurs resulting in constant, rather than decreasing, absorptivity.

Since it is not known to what extent the chemical lignin analysis measures oxidatively modified ring structures, it is not possible to ascribe the observed decrease in absorptivity (Table IV) to only *in situ* modified ring structures. In any event, it is probable some *in situ* modified lignin is present in ozonated FW. An upper limit of 20% can also be set for the amount of modified ring structures present in the residual lignin of ozonated FW.

Vander Linden (36), in his studies on chlorine dioxide modification of spruce groundwood, found *in situ* modification of lignin did occur. He estimated there were 22 ring-oxidized structures per 100 lignin equivalents in 6% chlorine dioxide treated groundwood.

Proposed Mechanism for Ozone-Degradation of Aromatic Rings in Lignin

The basic lignin structural unit in softwoods (i.e., loblolly pine) is the guaiacyl propane unit shown in Fig. 27 (50,51).

Since ozone is known for its electrophilic attack on electron-rich substrates, most notably carbon-carbon double bonds (6-8), it can be expected to react quite readily with the aromatic bonds present in lignin. A plausible mechanism, similar to that proposed by Soteland (18), for the ozone degradation of a guaiacyl propane lignin structural unit is presented in Fig. 28.

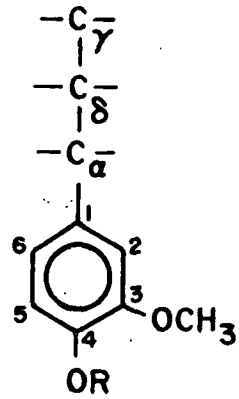

Figure 27. Guaiacyl Propane Structural Unit of Softwood Lignin

*Note — Throughout this thesis, the conventional notation shown above for the carbon atoms of the guaiacyl propane unit will be used

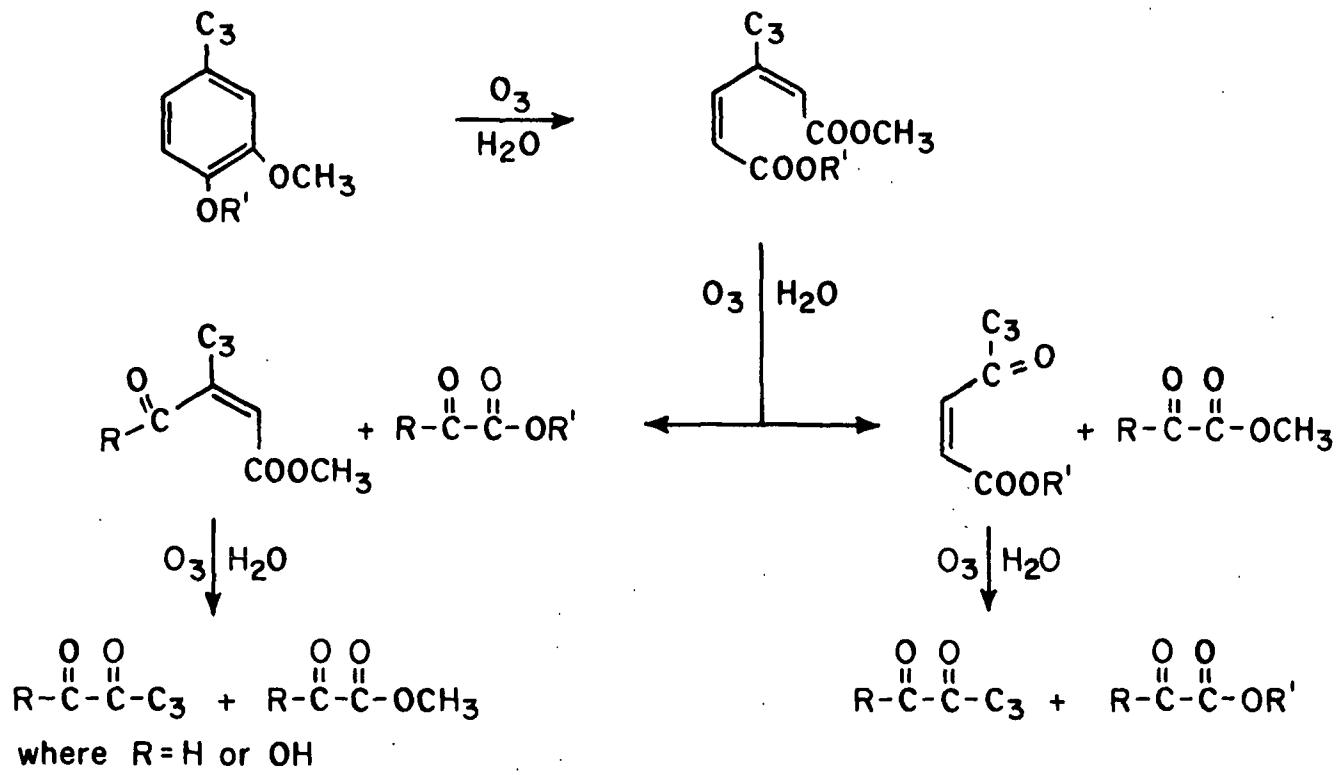

Figure 28. Possible Mechanism for Ozone Degradation of Guaiacyl Propane Lignin Unit

Based on model studies (9-12), the initial attack of ozone on the aromatic ring would most likely occur between carbons 3 and 4 of the guaiacyl propane structural unit (see Fig. 28). However, reaction also occurs at the other aromatic bonds (11).

The 1,3 dipolar addition of ozone results in cleavage of the aromatic ring and exposure of the more reactive olefinic bonds. Complete degradation of the aromatic ring (Fig. 28) results in consumption of 3 moles of ozone per guaiacyl propane unit.

Stoichiometry of Ozone-Lignin Reaction

In considering the reaction of ozone with alkali-fiberized wood, it was desirable to determine the stoichiometry of the ozone-lignin reaction. The stoichiometry found for the ozone-lignin reaction was then compared with the stoichiometry indicated for the proposed lignin degradation reaction shown in Fig. 28.

The stoichiometry of the ozone-lignin reaction was determined based on solubilized lignin and a guaiacyl propane lignin structural unit having an empirical formula of $C_9H_{8.5}O_{2.6}(OCH_3)_{0.96}$, corresponding to an equivalent weight of 188. The empirical formula represents an average guaiacyl propane structural unit in softwood lignin (52). The assumed equivalent weight of 188 agrees favorably with the value of 188.9 determined by Crozier (53) for loblolly pine dioxane lignin.

The stoichiometry determined for the reaction of lignin with ozone is given in Table V.

The stoichiometry of the ozone-lignin reaction remained relatively constant at all levels of ozone consumption, varying from 2.3-2.6 moles ozone con-

sumed/equivalent lignin solubilized. A plot of total lignin content versus ozone consumed (Fig. 29) indicated a linear relationship between lignin content and ozone consumption for reactions involving fiberized wood. These results suggest the same type of ozone delignification mechanism was operating at all levels of ozone consumption.

TABLE V

STOICHIOMETRY OF OZONE-LIGNIN REACTION[a] FOR ALKALI-FIBERIZED LOBLOLLY PINE

Ozone		Lignin Solubilized		Moles Ozone Consumed/ Equivalent Lignin Solubilized
%	Moles	g[b]	Equivalents[c]	
1.0	0.21	15	0.08	2.6
3.0	0.63	53	0.28	2.3
5.0	1.04	82	0.44	2.4
7.0	1.46	109	0.58	2.5

[a]All values on 1000 g o.d. fiberized wood basis.

[b]Based on results of Klason + acid-soluble lignin determinations (Table II).

[c]Assuming 188 g/guaiacyl propane lignin equivalent.

An average stoichiometry of 2.5 was obtained for the ozone-lignin reaction based on regression analysis of the total lignin contents (Fig. 29). Since the stoichiometry calculations were based on solubilized lignin, they represent maximums. Actual values would be somewhat lower since ozone consumption by in situ lignin and carbohydrate modification reactions and carbohydrate solubilization reactions was not taken into account.

In summary, the average stoichiometry of 2.5 found for the ozone-lignin reaction approaches the maximum stoichiometry of 3.0 shown in Fig. 28 for the

complete degradation of a guaiacyl propane unit. This suggests the degradation mechanism is possible and similar reaction mechanisms, resulting in the complete degradation of the guaiacyl propane unit, probably occur in the fiberized wood system. However, other side reactions involving lignin and carbohydrate also take place resulting in consumption of ozone. Since the amount of ozone consumed by the FW is constant in each reaction, this leaves less ozone to react with and solubilize the lignin. Thus the average stoichiometry value is lower (2.5) than the maximum value (3.0) hypothesized for the complete degradation of a C-9 unit.

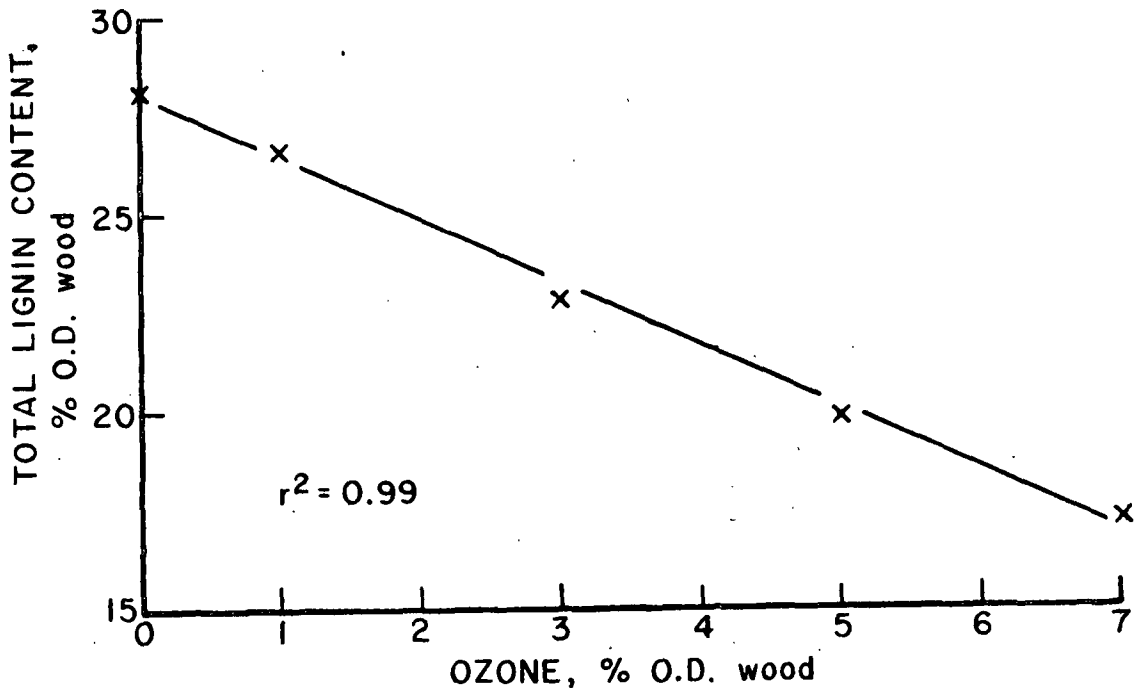

Figure 29. Total Lignin Content Versus Ozone Consumption for Alkali-Fiberized Loblolly Pine

Selectivity of Ozone-Lignin Reaction

The reaction of ozone with fiberized wood (FW) was also considered with respect to the selectivity of the ozone-lignin reaction. The successful use of ozone as a delignification or bleaching agent requires that it attack primarily lignin rather than carbohydrate.

The selectivity of the ozone-lignin reaction for ozone oxidation of FW was determined. The results are given in Table VI.

TABLE VI

SELECTIVITY OF OZONE-LIGNIN REACTION[a]
FOR ALKALI-FIBERIZED LOBLOLLY PINE

Ozone, %	Yield Loss, g	Solubilized Lignin, g[b]	Solubilized Carbohydrate, g[c]	Selectivity, %[d]
1.0	12	15	-3	100
3.0	67	53	14	79
5.0	92	82	10	89
7.0	143	109	34	76

[a]All values on 1000 g o.d. fiberized wood basis.

[b]Based on acid-soluble + Klason lignin content.

[c]By difference (yield loss − solubilized lignin = solubilized carbohydrate).

[d]Percent of total soluble material that is lignin.

The selectivities of 76-100% found for the ozone oxidation of FW showed lignin was preferentially degraded and solubilized by ozone treatment. This preferential attack is probably due to the abundance of aromatic and olefinic bonds in lignin, while no such bonds are present in the carbohydrate fraction of the wood. The carbon-carbon double bonds serve as reactive sites for electrophilic reagents such as ozone (6).

The lignin present in FW should also be more accessible than the carbohydrate, since the fiberization process was designed to expose primarily the middle lamella lignin of the fibers. Since the reaction of ozone with wood fibers has been shown to be largely a surface reaction (44,45), exposure of the middle lamella lignin should facilitate ozone's attack of the lignin.

The selectivity of the ozone-lignin reaction was a function of ozone consumption. At the 1% ozone level, only lignin was solubilized, but at the higher ozone levels significant amounts (11-24%) of the yield loss can be attributed to solubilized carbohydrate material.

Soteland (1,2) and Lindholm (29) estimated 75% of the yield loss for ozone-treated mechanical pulps was attributable to lignin degradation products and the remainder to carbohydrate material. These estimates agree well with selectivities of 79 and 76% obtained for this study (Table VI) at the 3 and 7% ozone consumption levels, respectively.

The decrease in selectivity at higher ozonation levels may have been caused by a reduction in lignin concentration on the fiber surface due to ozone oxidation. It is possible the ozone degradation of carbohydrate material does not become significant until a substantial amount of lignin on the fiber surface has been degraded, thereby exposing the underlying carbohydrate. As carbohydrate becomes more accessible and competition from lignin for the available ozone decreases, the degradation and subsequent solubilization of carbohydrate is facilitated.

It was previously found that the aromatic content of the lignin in FW decreased during the course of ozonation (Table IV). Since the electron-rich aromatic rings are prime sites for ozone attack, significant loss of these

structures (at higher ozonation levels) could shift more of the ozone attack to the carbohydrate component.

These explanations for the decrease in selectivity at the higher ozonation levels are not necessarily supported by previous findings which indicated a linear decrease in lignin content with ozone consumption (Fig. 29) and constant stoichiometry (Table V).

An alternative explanation is that carbohydrate modification reactions were occurring at the 1% ozone level, but not to the extent necessary to invoke solubilization of the carbohydrate material. Possible in situ carbohydrate modification was not considered in determination of the selectivity results shown in Table VI.

OZONE DEGRADATION OF FIBERIZED WOOD CARBOHYDRATES

The ozone degradation of the carbohydrate component of wood is important with respect to the use of ozone as a lignin oxidant. Excessive carbohydrate degradation and/or yield loss cannot be tolerated in most delignification or lignin modification processes (i.e., bleaching, pulping, pretreatment). Thus analysis of the effect ozone had on the carbohydrate fraction of FW was of importance in this study.

Lignin-Free Yield for Ozonated Fiberized Wood

The lignin-free yield for ozonated FW was calculated based on washed yield and total lignin content (Klason + acid-soluble). The calculations for lignin-free yield appear in Appendix IX. The lignin-free yields found for ozonated FW are given in Table VII.

TABLE VII

LIGNIN-FREE YIELD FOR OZONATED FIBERIZED WOOD

Ozone, %	Lignin-Free Yield, %
1.0	100.4
3.0	98.1
5.0	98.6
7.0	95.3

Lignin-free yield represents the carbohydrate component of fiberized wood. The yield values served as an estimate of the total carbohydrate material remaining in ozonated FW, based on the amount originally present in the untreated FW.

The previous section indicated 11-24% of the total yield loss (at 3, 5, and 7% ozone) was carbohydrate material (Table VI). The lignin-free yields (Table VII) put these results into the correct perspective. For example, 24% of the total yield loss at the 7% ozone level is carbohydrate. However, this corresponds to a carbohydrate loss of only about 5% based on the amount originally present in the untreated FW. Thus the lignin-free yields indicated only small amounts of the carbohydrate present in FW were solubilized by ozone treatment. These amounts increased slightly at the higher levels of ozonation. Carbohydrate solubilization may represent a substantial consumption of ozone.

Carbohydrate Content of Solubilized Material

The water-soluble material removed from the ozonated FW upon washing was isolated as described in the Experimental section. The isolated material was then analyzed for the presence of carbohydrates. The results of the carbohydrate analysis are shown in Table VIII.

TABLE VIII

CARBOHYDRATE CONTENT OF WATER-SOLUBLE MATERIAL[a]

Ozone, %	Xylan	Galactan	Mannan	Araban	Rhamnan	Total Hemi.[b]	Glucan	Total
5.0	4.2	2.5	2.6	2.4	0.2	11.9	1.2	13.1
7.0	2.7	0.6	1.0	3.5	0.01	7.81	0.2	8.01

[a]Values as a percentage of total water-soluble material.

[b]Total percentage of sugars associated with hemicellulose.

The carbohydrate contents determined for the water-soluble material verified carbohydrate solubilization occurred upon ozonation of FW. All of the sugars normally found in wood were solubilized to some extent. The sugars associated with hemicellulose represented over 90% of the total solubilized carbohydrate.

Glucose, the sugar associated primarily with cellulose, was the most ozone-resistant sugar (solubilized to the least extent) even though it represented about 68% of the total sugar content of FW. Moore, et al. (31) found glucose to be the most ozone-resistant sugar in studies involving ozonation of wood shavings.

The hemicellulose sugars were solubilized to a greater extent as a result of their greater physical accessibility. Most chemical reagents reach the hemicelluloses much more easily than the crystalline regions of cellulose (54). Schuerch, et al. (26,30,31) found ozone degrades the carbohydrate fraction of wood, but does not penetrate the cellulose crystallites.

The total solubilized carbohydrate value of 13.1% (Table VIII) for 5% ozone treatment agreed well with the calculated value of 11% solubilized carbohydrate (Table VII) based on washed yield and total lignin content.

At the 7% ozone treatment level, there was very poor agreement between the analytically determined value (8.01%) and the calculated value (24%) for total solubilized carbohydrate. It also appeared that more carbohydrate material was solubilized at the 5% ozone level than at 7% ozone.

This apparent anomaly was explained on the basis that more extensive degradation of the carbohydrate material occurred at the higher ozonation level (7%), resulting in formation of sugar fragments which were undiscernible by the analysis procedure.

Evidence for the ozone degradation of sugars into smaller, nonpolar fragments (55) was provided by the gas chromatograms obtained for the carbohydrate analyses (see Experimental section) which showed the presence of volatile components other than those corresponding to the sugars listed in Table VIII. The concentration of these "other components" was observed to increase at the 7% ozone level.

Carbohydrate Content of Untreated and Ozonated Fiberized Wood

The carbohydrate content of untreated and ozonated FW was determined using the analysis procedure described in the Experimental section. The results of the carbohydrate analyses are presented in Table IX.

All sugars associated with hemicellulose were found in slightly smaller amounts in ozonated FW, while glucose percentages remained essentially constant for both untreated and ozonated FW. These results again suggest the more amorphous hemicellulose in FW was degraded and solubilized by ozone treatment, while the crystalline cellulose remained relatively intact. Glucose again appeared to be the most ozone-resistant sugar.

TABLE IX

CARBOHYDRATE CONTENT OF UNTREATED AND OZONATED WOOD[a]

Ozone, %	Araban	Xylan	Galactan	Mannan	Total Hemi.[b]	Glucan	Total Sugars
0.0	1.2	6.5	2.3	11.8	21.8	46.1	67.9
3.0	0.8	6.1	2.1	11.7	20.7	45.7	66.4
7.0	0.8	5.7	1.8	11.3	19.6	46.5	66.1

[a]All values adjusted for washed yield and expressed as a percentage of o.d. fiberized wood.

[b]Total percentage of sugars associated with hemicellulose.

The total sugar contents found for ozonated FW follow the decreasing trend observed for lignin-free yield (Table VII), however the magnitude of the decrease was not as great. This was expected since the carbohydrate analysis does not include uronic acids which represent approximately 4% of untreated loblolly pine (56).

Calculating uronic acid, by difference, from the carbohydrate analysis results and the total lignin contents (Table III), gives values of 4.0, 4.2, and 2.7% for untreated and 3 and 7% ozonized FW, respectively. The lignin-free yield based on carbohydrate analysis and calculated uronic acid was 98.8 and 95.1% for 3 and 7% ozone, respectively. These values agree very well with lignin-free yields shown in Table VII.

Cuene Viscosity of Untreated and Ozonated Fiberized Wood

The cuene viscosities of holocellulose fractions isolated from untreated and ozonated FW were determined. Viscosity was of interest in this study because it provides an estimate of the average degree of polymerization of the

holocellulose in FW. A plot of viscosity versus ozone consumption for alkali-fiberized wood is shown in Fig. 30.

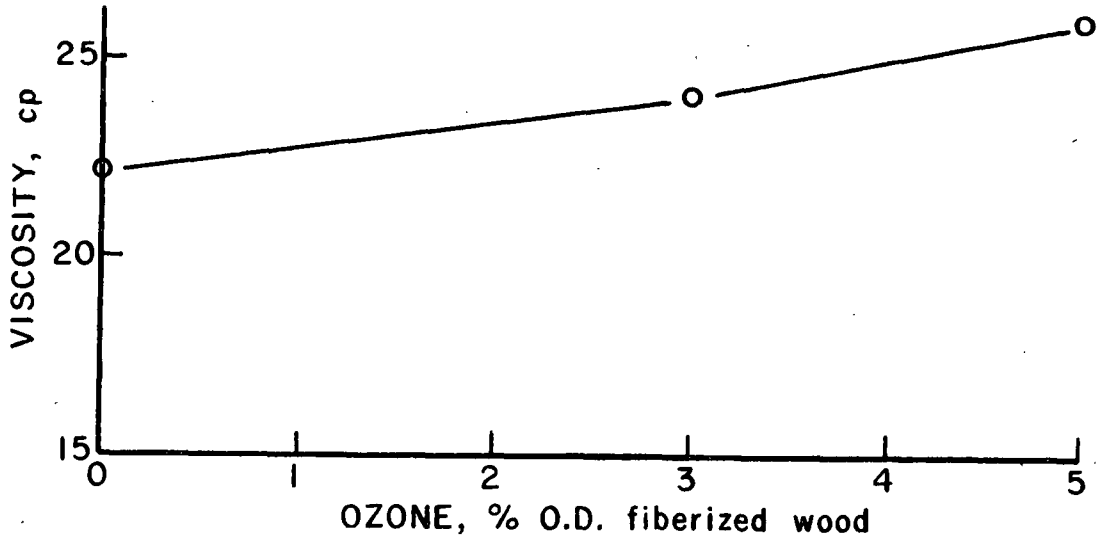

Figure 30. Cuene Viscosity Versus Ozone Consumption for Alkali-Fiberized Loblolly Pine

Slight increases in viscosity were found for holocellulose isolated from ozonated FW. These increases were indicative of small increases in the average degree of polymerization of the holocellulose.

Both lignin-free yields (Table VII) and carbohydrate analyses (Tables VIII and IX) showed some carbohydrate solubilization was occurring upon ozonation of FW. However, the degradation of carbohydrate to effect its solubilization must not involve excessive degradation of high DP native cellulose, but rather degradation and subsequent solubilization of lower DP hemicellulose. Thus the overall effect of hemicellulose solubilization was an increase in the average DP of the holocellulose isolated from ozonated FW.

Previously discussed results (carbohydrate analyses) have indicated hemicellulose material was solubilized to a much greater extent than cellulose, and

that cellulose percentages in ozonated FW were very similar to those of untreated FW.

Possible Mechanisms for Carbohydrate Solubilization

The reaction of ozone with fiberized wood has been shown to result in solubilization of carbohydrate material. Water-solubility requires that the carbohydrate polymer chains be reduced in size and/or oxygen functionalities incorporated into the chains to aid their solubility.

The carbohydrate analysis used in this study measures only total sugar content, not free sugars. Therefore, it is not possible to say if the solubilized sugars were present as monosaccharides or higher DP sugars (disaccharides, etc.). In any event, it is likely the water-soluble carbohydrates have a low DP, probably in the range of 5 or less (57).

The most common method of solubilizing the carbohydrates in FW would probably be through cleavage of the ether bond connecting two sugar units. Cleavage of this bond near the end of a polymer chain could result in freeing a chain fragment with low enough DP to be water soluble. Prior or further oxidation of this fragment with ozone would introduce oxygen functionalities aiding solubility of the chain fragment.

Mechanisms of ozone attack involving cleavage of the ether connecting linkage between two sugar units are therefore postulated as important for solubilization of carbohydrate. Chain cleavage in the holocellulose component of fiberized wood may occur via the ozone-catalyzed hydrolysis mechanism (Fig. 31) proposed by Katai and Schuerch (24) (see Background under Introduction).

proportional to the amount of lignin solubilized by ozone treatment (Appendix X). Thus brightness increase for ozonated FW was attributed primarily to lign solubilization, rather than lignin modification.

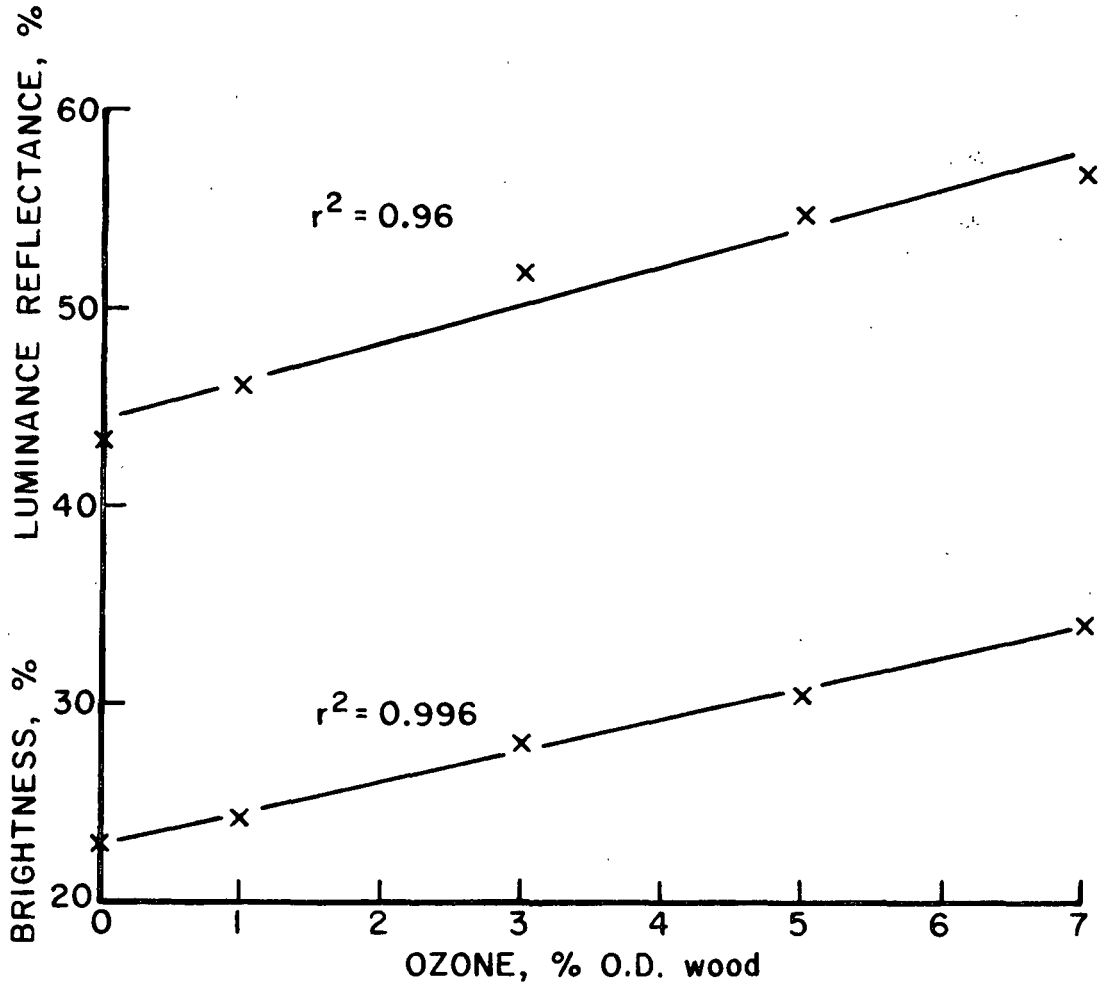

Figure 34. Brightness and Luminance Reflectance for Untreated and Ozone-Treated Alkali-Fiberized Loblolly Pine

The yield losses (Table II) found for ozonated FW were excessive in comparison to the small brightness gains. For example, the maximum brightness increase was 11 points at 7% ozone, while the corresponding yield loss was 14%.

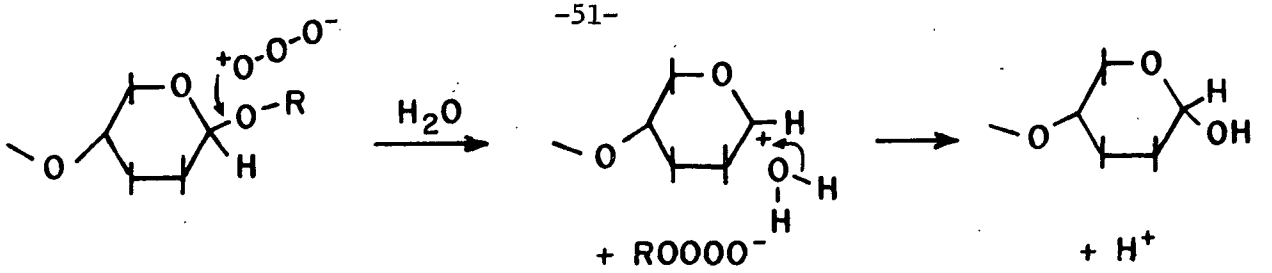

Figure 31. Chain Cleavage in Holocellulose of Fiberized Wood via Ozone-Catalyzed Hydrolysis Mechanism

Another plausible mechanistic route for chain cleavage is the 1,3 dipolar insertion mechanism as shown in Fig. 32. This mechanism was proposed by Bailey, et al. (21,58) for cleavage of ether linkages in organic materials.

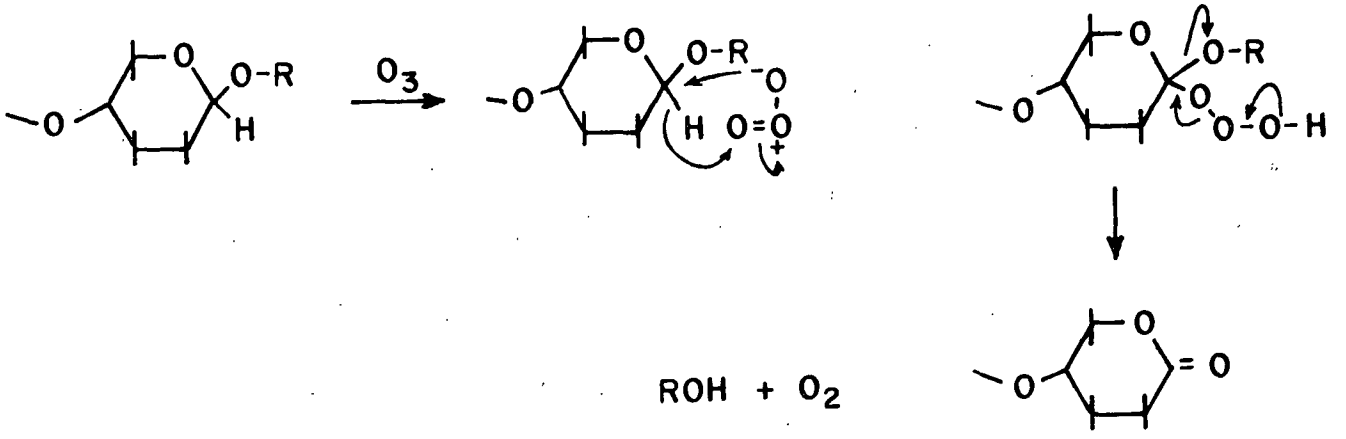

Figure 32. Carbohydrate Chain Cleavage via Ozone Insertion Mechanism

A third possible mechanism for chain cleavage involves ozone-initiated free-radical formation. Based on a mechanism proposed by Bailey (59) for ozonation of organic ether compounds, cleavage of the ether bonds in holocellulose might be envisioned as shown in Fig. 33.

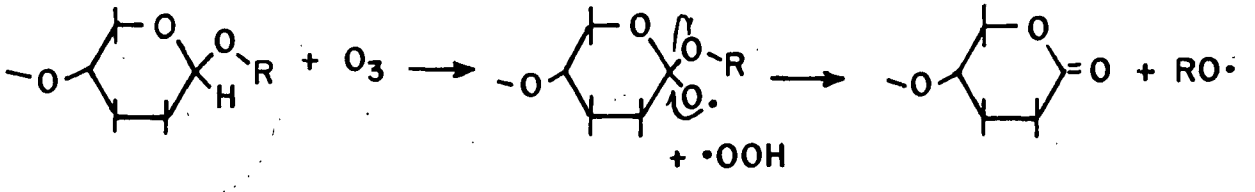

Figure 33. Chain Cleavage in Holocellulose of FW via Ozone-Initiated Free-Radical Mechanism

There was no experimental evidence for preference of any of the abovemen tioned mechanisms.

EFFECT OF OZONE ON FIBERIZED WOOD BRIGHTNESS

Sufficient pulp brightness is a necessary criterion in the manufacture of printing grades of thermomechanical and groundwood pulps. The bleaching of mechanical pulps to the necessary level of brightness relies on lignin modifying rather than lignin solubilizing bleaching agents.

Typical bleaching agents include sodium or zinc hydrosulfite, sodium bisulfite, and hydrogen and sodium peroxide (60). These chemicals act to modify the chromophores present in the pulp, thus increasing pulp brightness, while effecting relatively small yield losses.

The use of ozone as a mechanical pulp bleaching agent is of interest from an environmental standpoint since ozone is a nonpolluting oxidant. Basic requirements for such a process would include an increase in pulp brightness to at least 65%, no loss in pulp strength properties, and only small yield losses following ozone treatment.

It was shown that ozonation of FW results in significant delignification and yield loss, unless ozone consumption was kept in the neighborhood of 1% (based on o.d. FW). Strength properties (based on viscosity) of ozonated FW were found to remain essentially constant. The brightness and luminance reflectance of untreated and ozonated FW were determined. These results are shown in Fig. 34.

Only small brightness increases were observed for ozone-treated FW. A plot of brightness *versus* lignin solubilized showed brightness was directly

Therefore, use of ozone as a bleaching agent for mechanical pulps does not appear very promising unless small amounts are found to offer advantages when combined in other bleaching stages.

Lindholm (29) and Soteland (1-3) were unable to obtain any brightness increase for softwood mechanical pulps ozonated under conditions similar to those used in this study. They did find small brightness increases for ozonated hardwood mechanical pulps.

The reason brightness increases were observed in this study and not in previous work may be due to the presence of fewer heavy metal ions in the FW. Heavy metal ions such as iron, manganese, and copper are known to have a detrimental effect on ozone bleaching (4).

In this study the FW was soaked in dilute HCl to adjust its pH. This acid-soak may have resulted in removal of the trace metal ions initially present in the FW, thus facilitating bleachability of the wood.

The luminance reflectance (Fig. 34), which is measured at a higher wavelength than brightness (557 versus 457 nm), showed a slightly higher increase for ozonated FW as compared to untreated FW than the corresponding increase observed for brightness. The difference in relative increase between luminance reflectance and brightness was also more pronounced at the lower ozonation levels.

SUMMARY — TECHNICAL ASPECTS OF OZONE OXIDATION OF FIBERIZED WOOD

1. Gas-phase ozonation of alkali-fiberized loblolly pine resulted in rapid and almost complete (94-99%) consumption of ozone (at constant ozone flow rate).

2. Ozone treatment caused modification of the wood components. This modification made a portion of the wood water-soluble upon washing.

3. Yield losses (water-solubilized wood) ranged from 2-14% depending on the severity of the ozone treatment.

4. Both lignin and carbohydrate material were solubilized by ozone treatment. Lignin was preferentially solubilized as compared to carbohydrate. At least 76% of the water-soluble material was lignin derived.

5. The selectivity (based on percent lignin solubilized to total material solubilized) of the ozone-FW reaction decreased as ozone consumption levels were increased.

6. Ozone delignification resulted in solubilization of 5-39% of the lignin originally present in the fiberized wood. The extent of delignification was a function of ozone consumption.

7. It is probable some in situ lignin modification occurred in ozonated FW. Up to 20% of the aromatic rings present in the residual lignin of ozonated FW could have been oxidatively modified depending on the severity of the ozone treatment.

8. The stoichiometry of the ozone-lignin reaction was found to be 2.5 moles ozone consumed/equivalent guaiacryl propane unit solubilized.

9. Carbohydrate was also solubilized by ozone treatment of FW, but to a much lesser extent than lignin. Lignin-free yields ranged from 95-100%.

10. The majority (>90%) of the solubilized carbohydrate was hemicellulose material. Solubilization of low molecular weight hemicellulose resulted in small viscosity increases for ozonated FW due to an increase in the average DP of the holocellulose.

11. Ozone treatment of fiberized wood resulted in only small brightness increases. Brightness increase was attributed to lignin solubilization rather than lignin modification.

OZONE OXIDATION OF FIBERIZED WOOD
EFFECT ON SPECIFIC FUNCTIONAL GROUPS

The effect of ozone oxidation on the most common functional groups present in alkali-fiberized loblolly pine was determined. General information regarding ozone-induced changes in functional group content as well as mechanistic implications, based on the observed results, are discussed in the following sections.

METHOXYL

The methoxyl contents of untreated and ozonated FW were determined as described in the Experimental section. The results of the methoxyl determinations are given in Table X.

TABLE X

METHOXYL CONTENT OF UNTREATED AND OZONATED FIBERIZED WOOD

Ozone, %	Methoxyl, %[a]
0.0	4.85
1.0	4.58
3.0	3.91
5.0	3.64
7.0	3.30

[a]Based on untreated, o.d. fiberized wood.

The methoxyl content of 4.85% found for untreated FW compares favorably with the literature value of 4.81% obtained by Lewis (46) for loblolly pinewood. Over 90% of the methoxyl present in softwoods is found in the lignin (61). Small amounts of methoxyl are also present in the polysaccharides of wood, mainly as methoxy uronic acids (62).

The amount of methoxyl in untreated FW that is associated with lignin was estimated. Methoxyl is the most common functional group in lignin representing about 16% of softwood lignin (63-65). Crozier (53) found 15.99% MeO in loblolly pine dioxane lignin. Assuming untreated FW lignin also has a methoxyl content of 16%, it was calculated (based on methoxyl and lignin content found for untreated FW) that approximately 93% of the analytically determined methoxyl was present in the lignin of FW (see Appendix XI for calculation).

The methoxyl contents of ozonated FW were less than the methoxyl contents of untreated FW (Table X). Thus ozone oxidation of FW resulted in loss of methoxyl groups. The extent of the loss appeared to be a function of ozone consumption as shown in Fig. 35.

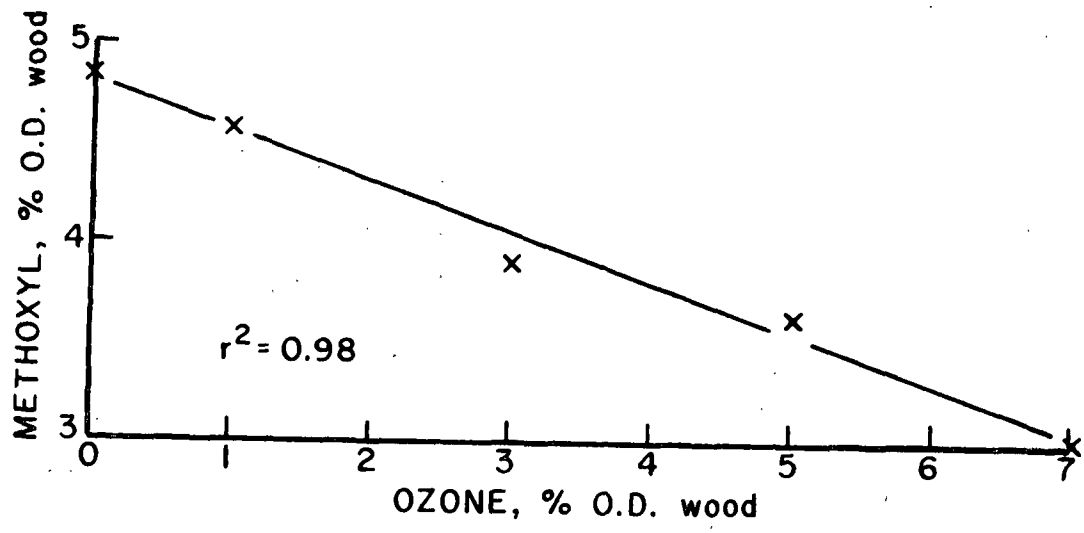

Figure 35. Methoxyl Content Versus Ozone Consumption for Alkali-Fiberized Loblolly Pine

Increasing ozone consumption resulted in increasing loss of methoxyl from FW. Methoxyl loss can be attributed to solubilization and/or in situ cleavage of the methoxyl groups through ozone treatment.

A rough estimate of the *in situ* effects of ozone oxidation on methoxyl present in FW lignin was obtained by calculating the methoxyl contents of the residual lignin in ozonated FW. An example of the calculation appears in Appendix XII. It was assumed 93% of the methoxyl measured for ozonated FW (Table X) was present in the lignin, based on the previously obtained estimate for untreated FW. The results for methoxyl content in ozonated FW lignin are shown in Table XI.

TABLE XI

ESTIMATED METHOXYL CONTENT IN OZONATED, FIBERIZED WOOD LIGNIN[a]

Ozone, %	Methoxyl, %
1.0	16.0
3.0	15.9
5.0	17.0
7.0	16.4

[a]Based on residual lignin content of ozonated FW and assuming 93% of methoxyl in FW is associated with lignin.

The methoxyl contents estimated for ozonated FW lignin remained near 16% (the value assumed for MeO content of untreated FW lignin) and stayed relatively constant regardless of ozone consumption. Thus, it was concluded *in situ* modification (demethoxylation and/or degradation) of the methoxyl groups in ozonated FW lignin probably did not occur to any significant extent, otherwise methoxyl contents for the FW lignin would have been substantially lower than 16%. Therefore, the loss of methoxyl observed upon ozonation of FW must be primarily a result of solubilization, rather than *in situ* modification, of this functional group.

Solubilized Methoxyl and Stoichiometry of Ozone-Methoxyl Reaction

The amount of methoxyl solubilized by ozone treatment of FW and the stoichiometry of the ozone-methoxyl reaction were determined for each level of ozone consumption. The results are given in Table XII.

TABLE XII

SOLUBILIZED METHOXYL AND STOICHIOMETRY OF OZONE-METHOXYL REACTION FOR OZONATED FW

Ozone, %	Solubilized Methoxyl, %[a]	Moles Ozone Consumed/ Equiv. MeO Solubilized
1.0	5.6	2.3
3.0	19.4	2.1
5.0	24.9	2.7
7.0	37.5	2.5

[a]Based on amount originally present in untreated fiberized wood

Ozonation of fiberized wood (FW) resulted in solubilization of methoxyl groups. Higher ozonation levels caused greater amounts of methoxyl solubilization.

The percent methoxyl solubilized, at each ozone level, approached the value obtained previously for percent lignin solubilized (Table III). Since approximately 97% of the guaiacyl propane units in loblolly pine lignin are estimated to contain a methoxyl group (53), solubilization of a C-9 unit could be expected to result in solubilization of the attached methoxyl group.

The stoichiometry of the ozone-methoxyl reaction found 2.1-2.7 moles ozone consumed per equivalent methoxyl removed. As expected, these values agreed

favorably with stoichiometry values obtained for the ozone-lignin reaction (Table V).

Reaction Scheme for Solubilization of Methoxyl Groups in Ozonated FW Lignin

Various model compound studies (9-12) indicated ozonation of the lignin model often resulted in retention of the methoxyl group in the degraded reaction. The methoxyl was characteristically retained as a methyl ester. In two cases (11,12), intact aromatic ring degradation products were recovered that had an unmodified methoxyl group.

Based on these findings and the fact that ozonation of FW resulted in solubilization of methoxyl groups, a plausible reaction scheme for solubilization of methoxyl groups in lignin was proposed as shown in Fig. 36. Other similar reaction sequences are also possible.

Structures I and II in Fig. 36 represent lignin degradation products having an intact aromatic ring with the methoxyl group still attached. The degradation route leading to products III, IV, and V is more probable and illustrates the formation of methyl esters (see Fig. 36).

Methoxyl Content of Water-Soluble Fraction of Ozonated Fiberized Wood

The methoxyl content of the water-soluble fraction of ozonated FW was calculated at each ozonation level. The actual methoxyl content of isolated, water-soluble material from 5 and 7% ozone-treated FW was determined for comparison. The results are shown in Table XIII. The procedures used to isolate the water-soluble reaction products are given in the Experimental section.

A decreasing trend was observed for calculated methoxyl content as ozone consumption levels were increased. One would expect a methoxyl content of approximately 16% for the water-soluble material if it represented only degraded

lignin material and if removal of a methoxyl group was accompanying solubilization of a C-9 unit. Since up to 24% of the water-soluble reaction products were found to be carbohydrate material (Table VI), the calculated methoxyl contents should be less than 16%. Therefore, the values obtained at 3, 5, and 7% ozone consumption seem reasonable if corresponding carbohydrate losses are considered.

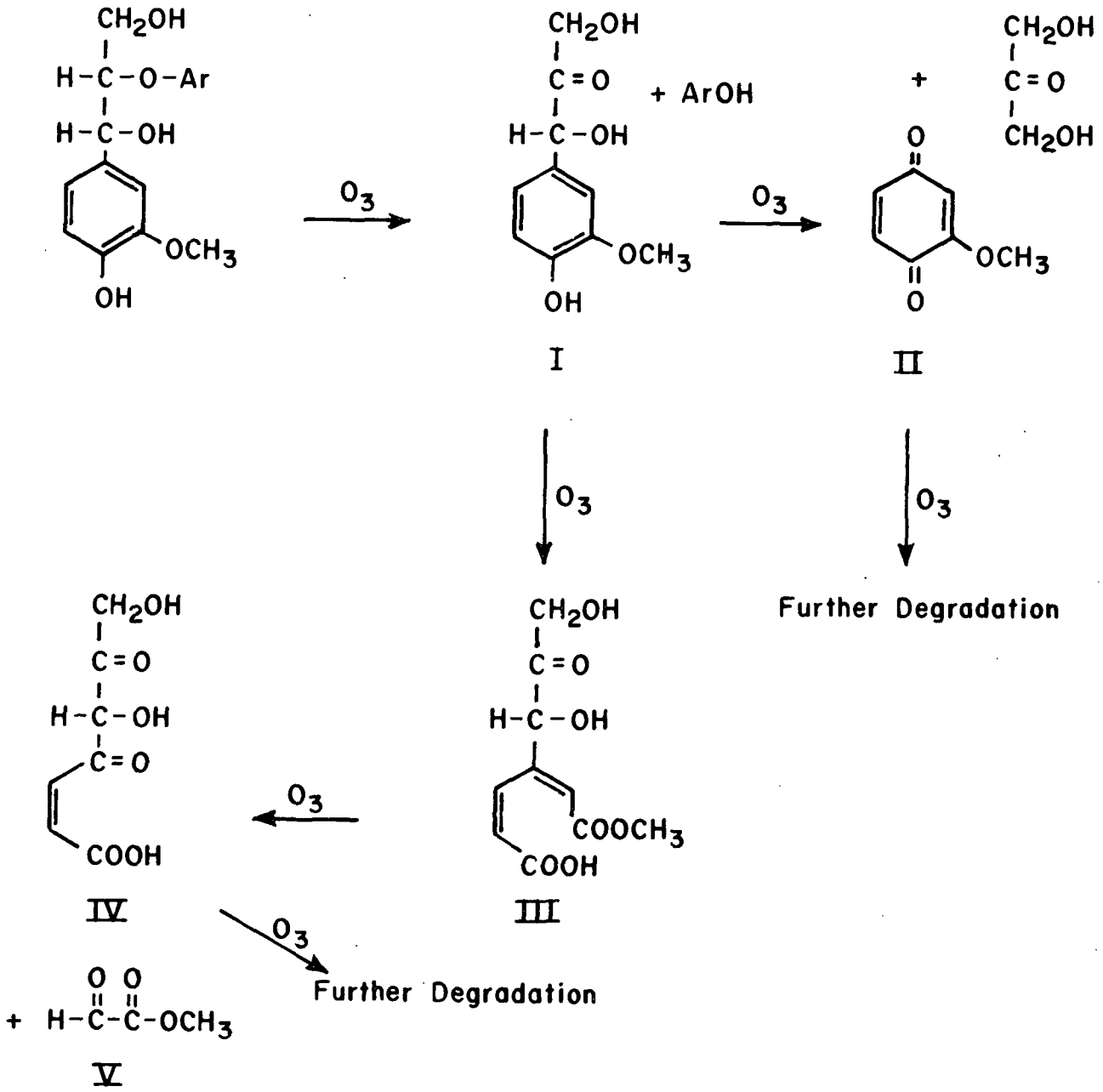

Figure 36. Possible Reaction Scheme for Solubilization of Methoxyl Groups in Lignin

TABLE XIII

CALCULATED AND ACTUAL METHOXYL CONTENT OF WATER-SOLUBLE FRACTION FROM OZONATED FIBERIZED WOOD

Ozone, %	Methoxyl Content of Water-Soluble Material, %[a]	
	Calculated[b]	Found
1.0	22.5	-
3.0	14.0	-
5.0	13.2	3.94
7.0	12.7	3.55

[a]Based on total solubilized material.

[b]Based on FW methoxyl content and washed yield (see Appendix XIII for calculation).

The value of 22.5% methoxyl calculated for the 1% ozone level (Table XIII) was rather high in comparison with the values obtained at the other ozonation levels. It is possible a specific demethoxylation mechanism, similar to that shown in Fig. 37, was operating at the low ozone consumption level, solubilizing methanol without the rest of the C-9 unit. However, this is purely speculation.

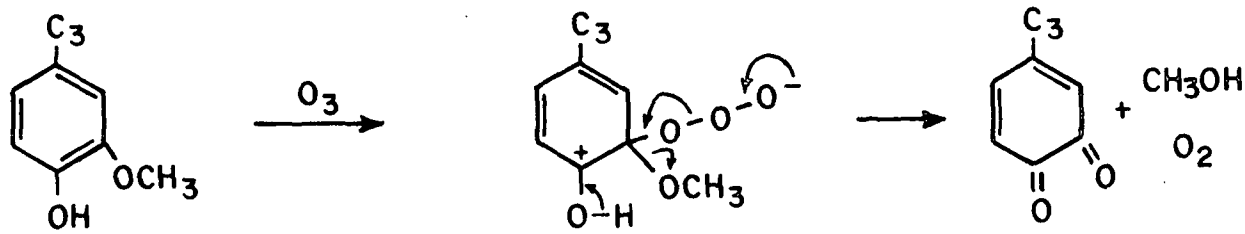

Figure 37. Electrophilic Substitution of Ozone Resulting in Demethoxylation of Guaiacyl Propane Unit at Low Ozone Consumption Levels

The actual methoxyl contents found for the water-soluble material (Table XIII) represented only about 30% of the calculated values. This indicated most of the methoxyl must have been present as rather volatile material that was subsequently lost in the vacuum concentration and freeze-drying processes used to isolate the water-soluble material.

Soteland (18) also found low concentrations (5-6%) of methoxyl for vacuum concentrated, acetone-water soluble fractions isolated from ozonized western hemlock groundwood.

Both methanol and low-molecular weight methyl esters would have the necessary volatility to be lost during the isolation process. Schuerch (24) isolated methanol as a volatile reaction product in the ozonation of α-methyl glucoside. Balousek (11) and Kojima, et al. (12) both isolated methyl esters from the ozonation of lignin model compounds.

Infrared spectra of the isolated, water-soluble reaction products (Appendix XIV) showed some aromatic absorbance. Therefore a portion of the detected methoxyl may also be present in unmodified form, on the intact, solubilized aromatic rings (see Fig. 36). Kojima and Balousek also recovered reaction products from their ozonations that had intact aromatic rings and unmodified methoxyl groups.

CARBOXYL

The extensive oxidation of organic materials characteristically yields carboxyl groups of some type. Since ozone is a strong oxidizing agent, the ozonation of fiberized wood could also be expected to produce carboxyl groups.

Formation of Carboxyl Groups in Ozonated Fiberized Wood

The carboxyl contents of untreated and ozonated FW were estimated using a conventional titration procedure (TAPPI Standard T 237). FT-IR difference spectroscopy was used to qualitatively follow the changes in carboxyl content. Reliable extinction coefficients were not available for calculation of carboxyl content from the FT-IR absorbance values.

The difference spectroscopy technique was similar to that used by Vander Linden (36) for estimating changes in carboxyl content for chlorine dioxide-treated spruce groundwood. An acidified wood spectrum (Appendix VI) was subtracted from a neutralized wood (pH = 9.2) spectrum (Appendix V), following balancing and conversion to absorbance, to obtain a difference spectrum (Appendix XV).

In an acidified wood spectrum all carboxyl appears as the acid (COOH) and absorbs in the infrared at 1725 cm^{-1}. In a neutralized wood spectrum all carboxyl appears as carboxylate anion (COO^-) and absorbs at 1605 cm^{-1}. The difference spectrum has a positive absorbance at 1605 cm^{-1} and a negative absorbance at 1725 cm^{-1}, both of which represent the carboxyl present in FW.

An example of a difference spectrum for neutralized FW minus acidified FW is shown in Fig. 38. Details of the FT-IR difference spectroscopy technique are covered in the Experimental section.

The results of the carboxyl analyses are given in Table XIV.

Leopold (47) found 20 meq carboxyl/100 g o.d. wood for untreated loblolly pine. The carboxyl content of 12.5 meq determined in this study for FW was significantly lower than the value determined by Leopold (47), possibly due to

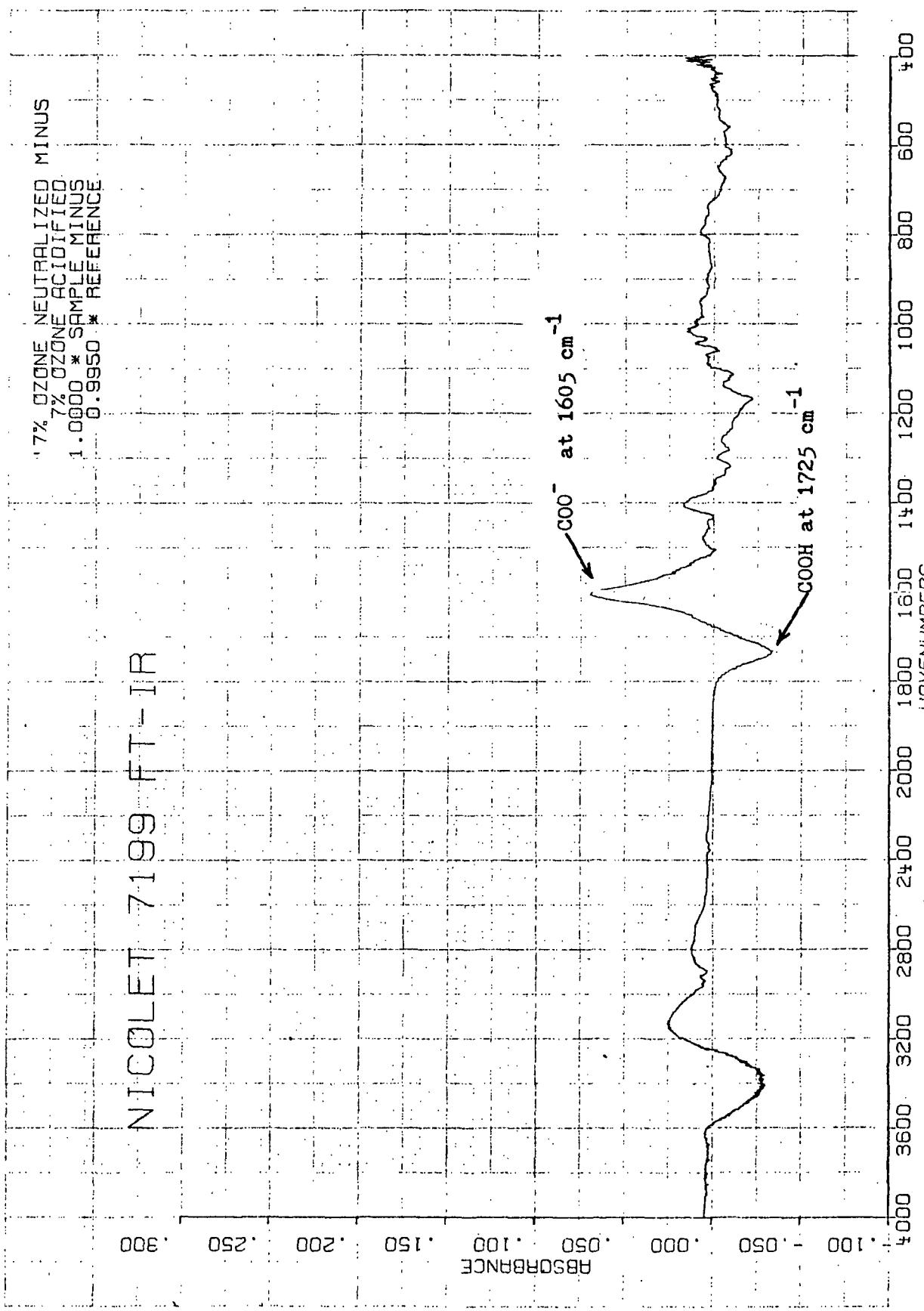

Figure 38. FT-IR Difference Spectrum of Neutralized FW Minus Acidified FW at 7% Ozone Consumption

the different analysis procedure or loss of carboxyl during the alkaline fiberization process.

TABLE XIV

CARBOXYL CONTENT OF UNTREATED AND OZONATED FIBERIZED WOOD

Ozone, %	TAPPI Carboxyl, meq/100-g o.d. wood	Absorbance[a]	
		Acid 1725 cm^{-1}	Salt 1605 cm^{-1}
0.0	12.5	-0.038	0.045
1.0	15.5	-0.033	0.063
3.0	15.4	-0.038	0.062
5.0	16.3	-0.037	0.062
7.0	15.8	-0.034	0.067

[a]From neutralized FW minus FW difference spectra (Appendix X).

Soteland (1,3) found 7.0 meq carboxyl/100 g o.d. wood for a thermomechanical pine pulp, using a dynamic ion-exchange analysis method. His result supports the hypothesis that fiberization results in some loss of carboxyl groups.

In general, the carboxyl contents (Table XIV) were found to be greater for ozonated FW than untreated FW and increased slightly at the higher ozonation levels. Increases of 23-30% were found for ozonated FW based on the TAPPI analysis procedure. The FT-IR difference spectroscopy technique showed increases in carboxyl content of 38-49% based on absorbance at 1605 cm^{-1}, while no increase was detectable for ozonated FW at an absorbance of 1725 cm^{-1}. The reason for this discrepancy in the difference spectroscopy results is not known, but could be caused by increasing noncarboxyl carbonyl content balancing the increasing carboxyl content. Another possibility is that some of the muconate structures, which could have formed upon ozonation, were hydrolyzed during the

neutralization process to their corresponding carboxylate salts. A third factor that could introduce error into the carboxylate absorbance values is the fact there is a slight overlap of the carboxylate anion (1605 cm^{-1}) and the aromatic stretching (1600 cm^{-1}) vibrations.

The trends observed for carboxyl increase in FW (Table XIV) are very similar when results from the TAPPI Standard method and the FT-IR difference spectroscopy method at 1605 cm^{-1} are compared. Soteland (3) found similar trends of increasing carboxyl content for ozonized thermomechanical pulp from pine. Kratzl, et al. (10) and Hatakeyama, et al. (14) both observed increasing carboxyl content for ozonated kraft lignin and calcium lignosulfonate, respectively.

The increase in carboxyl content found for ozonated FW cannot be attributed specifically to the lignin or carbohydrate component of the wood. Based on solubilized wood material, which was found to contain at least 76% lignin degradation products (Table VI), one could predict most of the carboxyl formation in FW probably involves lignin rather than carbohydrate. However, this is merely speculation.

Mechanisms for in situ Carboxyl Formation in Lignin and Carbohydrate Components of Ozonated Fiberized Wood

Possible mechanisms for in situ formation of carboxyl in lignin and carbohydrate components of ozonated FW are illustrated in Fig. 39-41. Most mechanisms in the literature show end-products of ozone oxidations as carbonyls (usually aldehydes) rather than carboxyls. It should be mentioned that further oxidation of the aldehyde group (as shown in Fig. 39-41) is very possible in the FW system. An ozone-oxygen atmosphere prevails in the reactor, thus facilitating auto-oxidation of aldehyde groups by molecular oxygen or further oxidation with ozone. The ozone-FW reaction occurs under acidic conditions, water is present, and small

amounts of peroxides and free-radicals have probably been generated which would aid further oxidation of aldehydic functionalities to carboxyl groups.

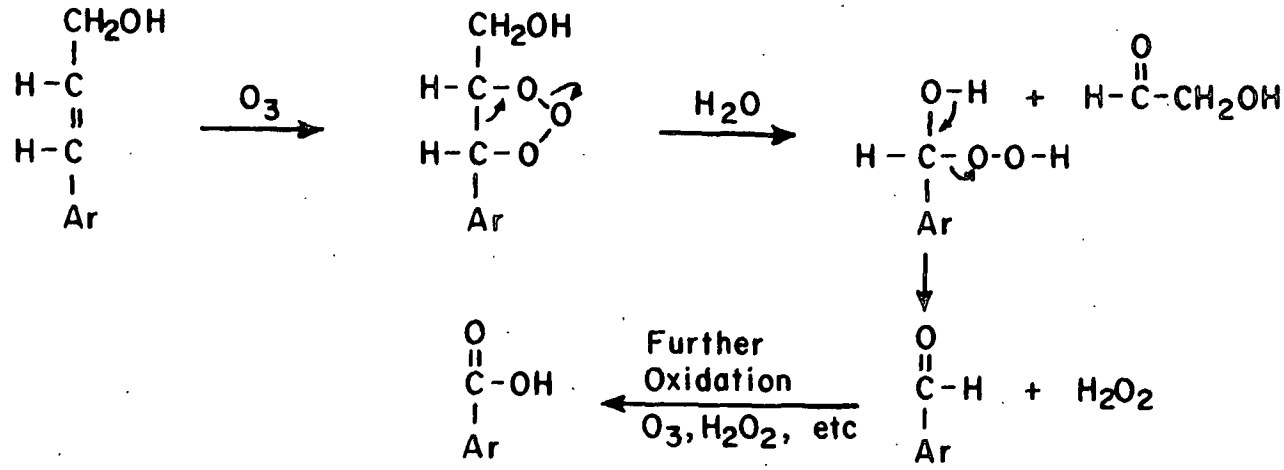

Figure 39. Ozone Oxidation of Olefinic Side-Chain Structure in Lignin to Form Carboxyl Group

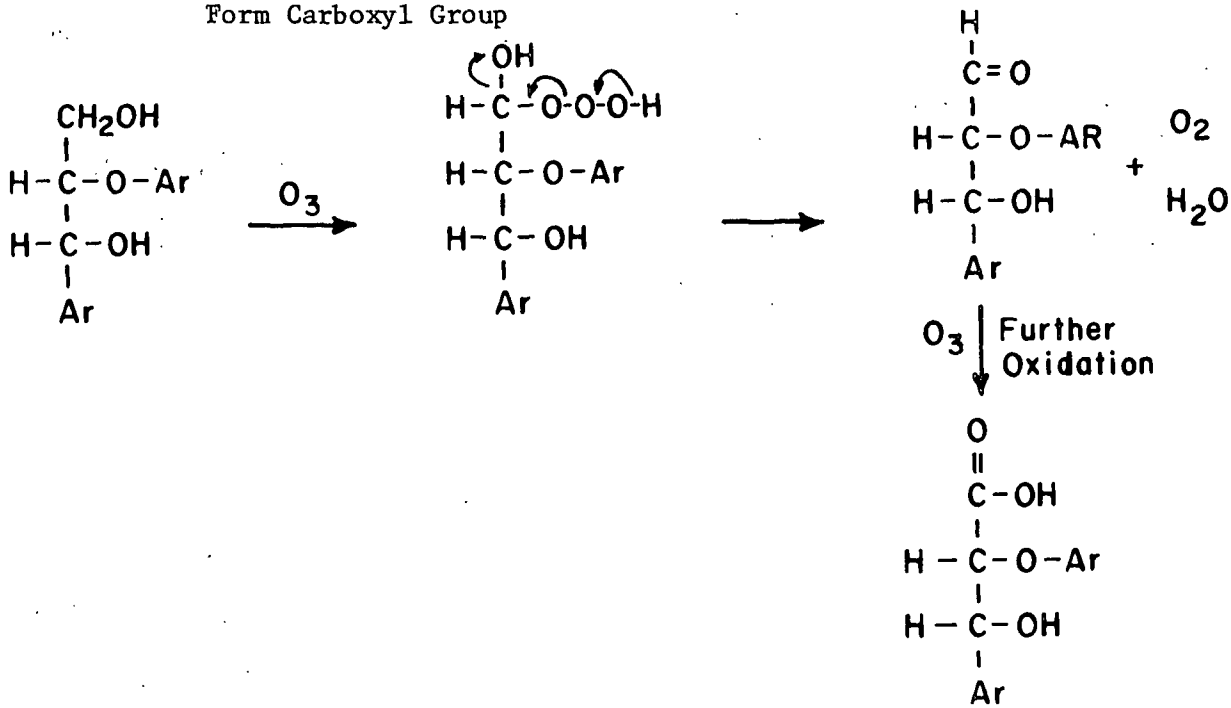

Figure 40. Ozone Oxidation of γ-carbon on Lignin Side-Chain via Ozone Insertion Mechanism

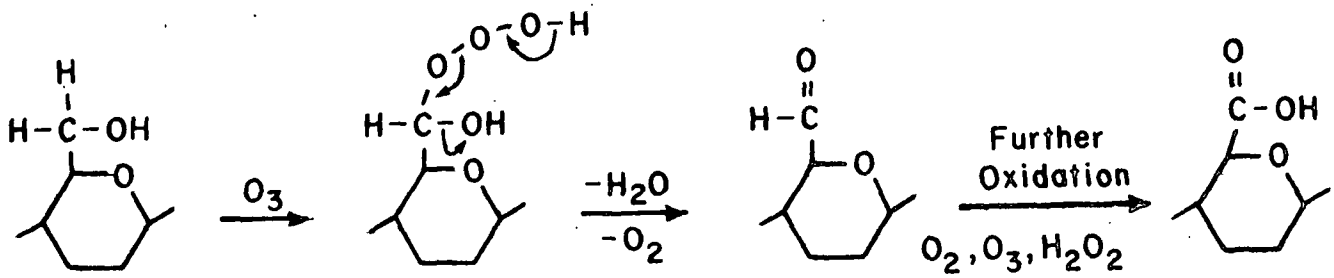

Figure 41. Ozone Oxidation of Carbohydrate via Ozone Insertion Mechanism to Form Carboxyl Group at C-6

The above mechanism is analagous to the ozonolysis mechanism proposed by Criegee (8) for oxidation of olefins (Fig. 39).

Magnitude of Carboxyl Production for the Ozone-Fiberized Wood Reaction

The amount of insoluble and water-soluble carboxyl produced at each level of ozone consumption was determined for the ozone-FW reaction. The results are given in Table XV.

TABLE XV

CARBOXYL PRODUCTION FOR OZONE-FIBERIZED WOOD REACTION

	Carboxyl Produced (meq/100-g o.d. FW)				
Ozone, %	Insoluble[a]	Water-Soluble[b]	Total Produced	Water-Soluble/ Total Produced[c]	Meq Produced/MM, Ozone Consumed
1.0	3.0	5.0	8.0	63	0.38
3.0	2.9	41.2	44.1	93	0.70
5.0	3.8	77.6	88.4	95	0.78
7.0	3.3	102.6	105.9	97	0.73

[a] Based on TAPPI Std. results (Table XV).

[b] Carboxyl content of wash filtrate as determined by potentiometric titration.

[c] Percentage of total carboxyl produced that is water-soluble.

Rapidly increasing amounts of water-soluble carboxyl were generated in the reaction of FW with ozone, as ozone consumption levels increased from 1 to 7%. In comparison, the amount of *in situ* (insoluble) carboxyl formed in the ozonated FW was quite low and remained relatively constant regardless of the ozone consumption level.

The ratio of water-soluble carboxyl produced to total carboxyl produced was found to rapidly increase at the higher ozonation levels (3, 5, and 7%), where over 90% of the total carboxyl produced was water soluble.

This indicated continued degradation of the wood components into smaller, water-soluble fragments containing carboxyl functional groups was occurring. Incorporation of carboxyl functionalities into the degraded FW fragments increases their water solubility.

The milliequivalents of carboxyl produced per millimole of ozone consumed (Table XV) showed carboxyl formation was the dominant reaction in the ozonation of FW, except at the 1% ozone level. At the higher ozone consumption levels approximately 70-80% of all the ozone consumed by FW resulted in carboxyl formation of some type.

A plot of total carboxyl produced versus ozone consumption for reactions with fiberized wood is shown in Fig. 42.

Figure 42 graphically illustrates the rapid production of carboxyl groups upon ozonation of FW. The line appearing in the graph is a result of regression analysis and indicates there is a linear relationship between carboxyl produced and ozone consumed. The low value for carboxyl at 1% ozone is consistent with the nonzero intercept.

Partial Chemical Characterization of the Acidic Water-Soluble Reaction Products

The initial pH of untreated FW in distilled water was found to be 6.6. The wash filtrates from ozonated FW had pH values that ranged from 2.1-2.8 depending on the severity of the ozone treatment. This suggested acidic, water-soluble reaction products were being formed by ozone treatment of FW.

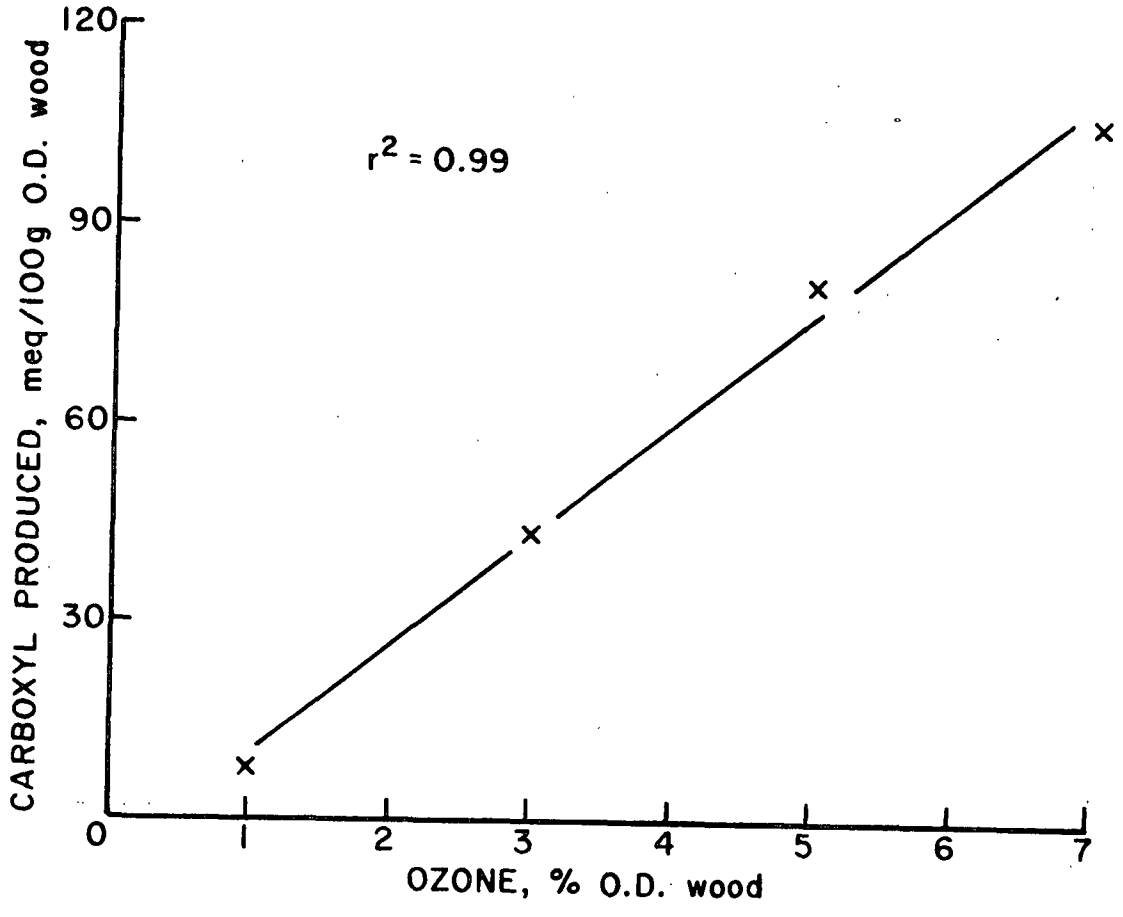

Figure 42. Total Carboxyl Produced versus Ozone Consumption for Reaction of Fiberized Wood With Ozone

The previous section verified this assumption and showed large amounts of water-soluble carboxyl were formed when FW was oxidized with ozone. However, the chemical nature of this carboxyl material was not discussed.

Samples of water-soluble reaction products were isolated at the 5 and 7% ozone levels, as described in the Experimental section, and infrared spectra obtained. The spectra (Appendix XIV), as expected, showed evidence for the presence of large amounts of carboxylic acids.

There was a very intense absorption at approximately 1720 cm^{-1}, which is characteristic of the carbonyl stretching mode in saturated aliphatic acids (66,67). A broad and intense absorption band at 3300-3500 cm^{-1} was also present. This band was assigned to the O-H stretching vibration of hydroxyl groups in carboxylic acids (67).

Gas-chromatographic analysis (see Experimental section for procedure) indicated 10% of the total water-soluble material isolated at the 5% ozone level was oxalic acid. This corresponds to approximately 20-meq acid/100 g o.d. FW, thus representing about 25% of the total water-soluble acid found at 5% ozone consumption (see Table XV).

The peak attributable to oxalic acid was the largest in the chromatogram, but other peaks representing similar carbonyl compounds (glyoxylic acid, etc.) were also present (see Experimental section for gas chromatogram).

Soteland (18) had previously isolated oxalic acid from western hemlock groundwood ozonized in acetone-water solution (9:1). Hatakeyama, et al. (14) isolated both oxalic and maleic acids from ozonated calcium lignosulfonate. Balousek (11) identified 2,3-dihydroxybutric acid as a degradation product from ozonation of a β-aryl ether lignin model, while Kojima, et al. (12) detected both oxalic and vanillic acids in his study on ozone oxidation of softwood lignin models.

Oswa, et al. (30) and Moore, et al. (31) had also suggested the formation of formic and acetic acids based on their ozone pulping experiments. Thus, the ozone oxidation of FW probably resulted in the formation of many different carboxylic acids due to the complexity of the substrate.

Oxalic acid seemed to be the most abundant acid formed in the FW system at 5% ozone, but other carboxylic acids that might have been present in greater amounts, could have easily gone undetected. Volatile acids such as formic and acetic could have been lost during the vacuum concentration and freeze-drying process used to isolate the reaction products.

The generation of significant amounts of oxalic acid could pose a problem in commercial ozone bleaching processes if the bleach liquor is recycled back to the recovery system. The liquor may promote the formation of oxalate scale.

CARBONYL

Formation of carbonyl functionalities is an expected consequence of ozone oxidations involving organic materials such as wood (see Background under Introduction). For this reason, analysis of the changes in amount and type of carbonyl groups found for ozonated FW was of importance to this study.

FT-IR difference spectroscopy was used for carbonyl analysis of untreated and ozonated FW. As mentioned in Experimental Approach, it was necessary to assume the wavelength of absorbance and the extinction coefficients remained relatively constant, regardless of changes induced in their chemical environment through ozonation. Based on limited literature values for simple carbonyl compounds (68-70) and a previous study (35) involving use of difference spectroscopy for carbonyl analysis of lignin, it was felt this was a justified assumption. Further details of the FT-IR difference spectroscopy analysis technique are given in the Experimental section and Appendix I.

Several types of difference spectra were obtained in this study, each of which provided specific information on certain general classes of carbonyl com-

pounds. The various types of difference spectra and the information they provide concerning carbonyl functionalities are summarized below.

1. Ozonized, unwashed FW minus untreated FW difference spectra (Appendix VII). Indicate total carbonyl produced by ozonation of fiberized wood (FW).
2. Ozonized, washed FW minus untreated FW difference spectra (Appendix VII). Indicate in situ effect of ozone on total carbonyl content of fiberized wood.
3. Ozonized, unwashed FW minus ozonized, washed FW difference spectra (Appendix VII). Provide indication of water-soluble carbonyl formed by ozonation of FW.
4. Ozonized, washed neutralized FW minus untreated, neutralized FW difference spectra (Appendix VIII). Provide for analysis of noncarboxyl carbonyl in ozonated FW.

This study was concerned with both unconjugated and conjugated carbonyl groups. Unconjugated carbonyl functionalities are covered in the first part of this section, and conjugated carbonyl in the latter.

Unconjugated Carbonyl

The unconjugated carbonyl groups were represented in the infrared difference spectrum of FW by absorbance at approximately 1730 cm^{-1}. This frequency is characteristic of the C=O stretching vibration of the carbonyl group (67,71). Carbonyl compounds absorbing near this frequency include saturated carboxylic acids, ketones, aldehydes, and esters (67,71).

The unconjugated carbonyl absorbance values obtained from the FT-IR difference spectra (Appendix VII) are shown in Table XVI. The absorbance values for

total carbonyl and insoluble carbonyl represent absorbance in excess of that originally present in untreated FW.

TABLE XVI

UNCONJUGATED CARBONYL ABSORBANCE AT 1730 CM^{-1}

Ozone, %	Total[a] Carbonyl	Insoluble[b] Carbonyl	Water-Soluble[c] Carbonyl	Water-Soluble/ Total Carbonyl, %
1.0	0.033	0.022	0.011	33
3.0	0.082	0.039	0.043	52
5.0	0.145	0.051	0.094	65
7.0	0.235	0.067	0.168	71

[a]Based on FT-IR difference spectra of ozonized, unwashed FW —untreated FW.

[b]Based on FT-IR difference spectra of ozonized, washed FW — untreated FW.

[c]By difference, Total carbonyl — Insoluble Carbonyl = Water-Soluble Carbonyl.

The positive absorbance values obtained from the difference spectra indicated unconjugated carbonyl functionalities were formed by ozone oxidation of fiberized wood. Higher ozonation levels resulted in larger absorbance values, corresponding to formation of greater amounts of carbonyl.

Both insoluble and water-soluble carbonyl groups were formed by ozone treatment of FW. A portion of the increase found for insoluble carbonyl was attributed to *in situ* carboxyl formation, based on previous results which showed an increase in carboxyl content for ozonated FW (Table XIV). However, the increases in ozonated FW carboxyl content were found to remain relatively constant, regardless of the ozone consumption level. Thus the absorbance increases observed for insoluble carbonyl, at least at the higher ozonation levels, must be due in part to formation of noncarboxyl carbonyl compounds.

The water-soluble carbonyl absorbance (Table XVI) showed the same increasing trend as observed previously for water-soluble carboxyl (Table XV). Thus a portion of the water-soluble carbonyl absorbance was attributed to the formation of water-soluble carboxylic acids. Various noncarboxyl carbonyl compounds (ketones, aldehydes, esters) were responsible for the remaining absorbance.

Soteland (18) proposed the final degradation products of ozonized aromatic rings in lignin were glyoxal and glyoxylic acid derivatives, most of which are quite water soluble.

The ratio of water-soluble carbonyl to total carbonyl (Table XVI) was found to increase with ozone consumption. The water solubility of carbonyl functionalities produced during ozone oxidation of FW can be increased in two ways: (1) through further degradation of the wood structural component containing the carbonyl group(s) resulting in a smaller, now water-soluble fragment and/or (2) incorporation of additional polar groups (carbonyls, hydroxyls, etc.) into the structure, further increasing its water solubility.

The trend of increasing water solubility found for carbonyl (Table XVI) parallels the trend found for carboxyl (Table XV). However, the magnitude of the increase for carboxyl (63-97%) was greater than that found for carbonyl (33-71%). This again suggested increasing formation of *in situ* noncarboxyl carbonyl in ozonated FW.

Unconjugated, Noncarboxyl Carbonyl Formation in Ozonated Fiberized Wood

It was shown that ozonation of FW resulted in the *in situ* formation of carboxyl groups. The previously discussed results also strongly suggested the formation of noncarboxyl carbonyl groups in ozonated FW.

Absorbance values obtained from neutralized FW difference spectra serve as an indication of the noncarboxyl carbonyl functionalities formed in ozonated FW, as the absorption of carboxyl carbonyl shifts from 1730 to 1605 cm^{-1} upon neutralization (see Carboxyl section). Table XVII gives the absorbance values found for unconjugated, noncarboxyl carbonyl and the previously determined values for total insoluble unconjugated carbonyl.

TABLE XVII

IN SITU UNCONJUGATED CARBONYL ABSORBANCE AT 1730 CM^{-1}

Ozone, %	Noncarboxyl + Carboxyl[a]	Noncarboxyl[b]
1.0	0.022	0.017
3.0	0.039	0.019
5.0	0.051	0.024
7.0	0.067	0.034

[a] Values from ozonized, washed FW minus untreated FW difference spectra.

[b] Values from ozonized, washed, neutralized FW minus untreated neutralized FW difference spectra.

The absorbance values for noncarboxyl carbonyl were less than those found for total carbonyl (noncarboxyl + carboxyl) at corresponding levels of ozone consumption. This verified that both noncarboxyl and carboxyl carbonyl groups were formed in ozonated FW.

A direct comparison between noncarboxyl and total carbonyl absorbance cannot be made since the extinction coefficients of carbonyl and carboxyl are different (68-70). However, as the extinction coefficients of noncarboxyl carbonyl are less than those of carboxyl carbonyl, the conclusion is still valid.

It was previously observed (Table XIV) that the increase in carboxyl content of ozonated FW was approximately the same, regardless of ozone consumption level. Noncarboxyl carbonyl formation did not follow this trend. It was observed to steadily increase as ozone consumption was increased (Table XVII).

Unconjugated, noncarboxyl carbonyl formation in ozonated FW cannot be attributed specifically to lignin or carbohydrate reactions with ozone. However, carbonyl formation that did involve lignin was limited to the β- or γ-carbons of the propane side chain. Carbonyl groups formed at the α-carbon would be in conjugation with the aromatic ring and, with the possible exception of a few esters, would not absorb in the infrared at 1730 cm^{-1}.

Mechanistic Implications

The formation of unconjugated, noncarboxyl carbonyl groups in FW most likely proceeds via an ozone insertion mechanism. As mentioned previously, this mechanism involves attack of ozone at the carbon-hydrogen bonds of alcohols and ethers, resulting in carbonyl formation at the carbon of attack (21,22,58). Ozone-initiated free-radical formation could also be considered a possible mechanistic route for formation of unconjugated, noncarboxyl carbonyl functionalities in FW (see Background under Introduction).

Unconjugated, noncarboxyl carbonyl formation in FW lignin involved production of ketone, ester, and/or aldehyde functionalities on the β- and γ-carbons of the propane side chains. Several examples of the types of unconjugated carbonyl structures that might be expected to form upon ozone-oxidation of lignin are shown in Fig. 43.

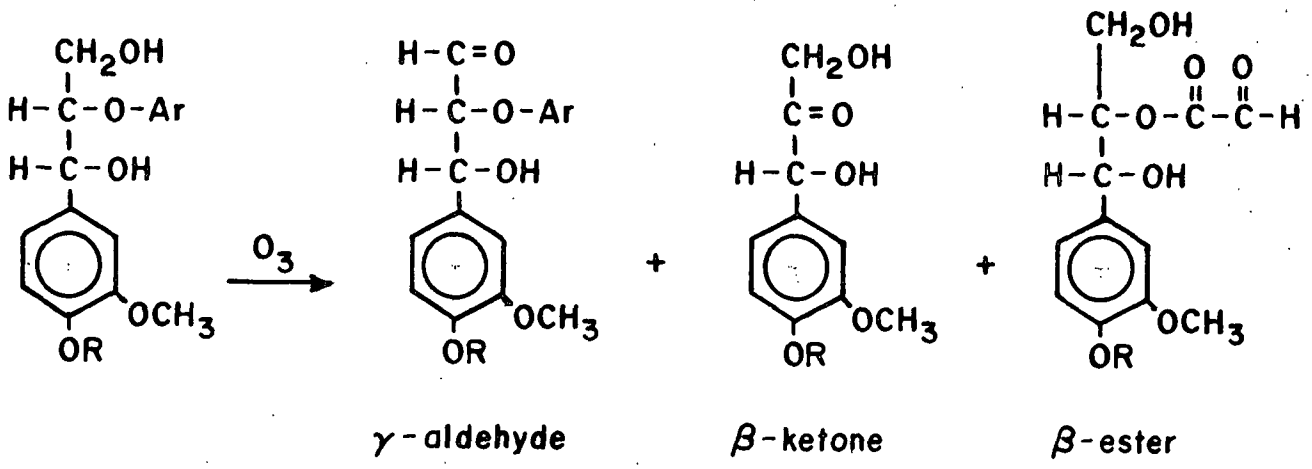

Figure 43. Possibilities for Unconjugated, Noncarboxyl Carbonyl Formation in Lignin of Ozonated Fiberized Wood

Balousek (11) and Kojima, et al. (12) each isolated reaction products from the ozonation of β-aryl ether lignin models that had unconjugated, noncarboxyl carbonyl groups present on the side chains of the aromatic rings (see Background under Introduction).

Noncarboxyl, unconjugated carbonyl formation in the holocellulose fraction of ozonized FW involved production of ketone, aldehyde, and/or lactone functionalities as illustrated in Fig. 44.

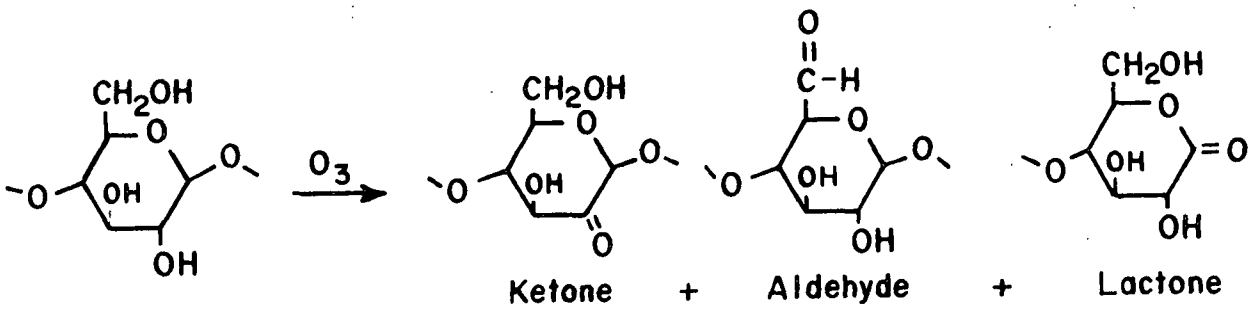

Figure 44. Possibilities for Unconjugated, Noncarboxyl Carbonyl Formation in Holocellulose of Fiberized Wood

Estimate of Increase in Unconjugated, Noncarboxyl Carbonyl Content of Ozonated Fiberized Wood as Compared to Untreated Wood

The absorbance value (at 1730 cm^{-1}) determined from the infrared transmission spectrum of neutralized, untreated FW (Appendix VIII) provided an estimate of the unconjugated, noncarboxyl carbonyl absorbance for untreated FW (see Experimental for procedure used to convert transmission spectrum to absorbance). This absorbance value was used in conjunction with the previously determined absorbance values (Table XVII), for ozonated, neutralized FW difference spectra, to calculate normalized spectra (see Experimental for further details of normalizing process).

The calculated absorbance values for the normalized spectra are given in Table XVIII. The absorbance values determined for the transmission and difference spectra are also included.

TABLE VIII

UNCONJUGATED, NONCARBOXYL CARBONYL ABSORBANCE AT 1730 CM^{-1}[a]

Ozone, %	Transmission Spectrum	Difference Spectrum	Normalized[b] Spectrum
0.0	0.016	-	0.016
1.0	0.038	0.017	0.033
3.0	0.035	0.019	0.035
5.0	0.037	0.024	0.040
7.0	0.042	0.034	0.050

[a] All values based on spectra obtained from neutralized FW samples.

[b] 0.016 + absorbance value from difference spectrum.

The transmission and normalized spectra both showed a significant increase in noncarboxyl carbonyl absorbance for ozonated FW as compared to untreated FW.

Higher levels of ozonation caused greater increases in noncarboxyl carbonyl absorbance.

The transmission spectra showed approximately the same trend as the normalized spectra. There was less error in the normalized spectra, since they were based on difference spectra which were balanced to correct for intensity variations between the FW samples used in the infrared analysis.

As mentioned previously, it was not possible to attribute the increase in unconjugated, noncarboxyl carbonyl to ozone reactions involving primarily lignin rather than carbohydrate. However, based on selectivity considerations (Table VI) one could predict the majority of the ozone-FW reaction involved lignin.

Assuming unconjugated, noncarboxyl carbonyl formation in ozonated FW involved only lignin, it was possible to roughly estimate the increase in unconjugated, noncarboxyl carbonyl content of the ozonated FW lignin. This was done by comparing the absorptivities (at 1730 cm^{-1}) calculated for the untreated and ozonated FW samples. The absorptivities were calculated from normalized spectra results (Table XVIII) and the lignin content of each sample. The results are given in Table XIX.

The absorptivities calculated for ozonated FW were significantly higher than that of untreated FW. This indicated greater amounts of unconjugated, noncarboxyl carbonyl groups were present in the residual lignin of ozonated FW. Increases in carbonyl content were also observed to be greater for the more highly ozonized fiberized wood.

Based on the absorptivities (Table XIX) it was estimated a maximum of 2-4 times more unconjugated, noncarboxyl carbonyl was present in the residual lignin of ozonated FW as compared to untreated FW. This estimate represents a maximum

since some of the carbonyl formation undoubtedly involved carbohydrate, especially at the higher ozonation levels.

TABLE XIX

UNCONJUGATED, NONCARBOXYL CARBONYL ABSORPTIVITY

Ozone, %	Normalized[a] Absorbance	Lignin, mg[b]	Absorptivity, (Absorbance/ mg lignin)
0.0	0.016	0.281	0.057
1.0	0.033	0.269	0.123
3.0	0.035	0.244	0.143
5.0	0.040	0.219	0.183
7.0	0.050	0.201	0.249

[a]At 1730 cm^{-1}, based on normalized spectra of neutralized FW.

[b]Klason + acid-soluble lignin, based on 1-mg sample o.d. FW.

Conjugated Carbonyl

The conjugated carbonyl groups were represented in the FT-IR difference spectra of FW by absorbance at approximately 1660 cm^{-1}. This frequency is characteristic of the C=O stretching vibration of conjugated carbonyl groups (67,71).

Absorbance at 1660 cm^{-1} represented carbonyl associated only with lignin, since there are no olefinic or aromatic bonds in carbohydrates for the carbonyl group to be in conjugation with.

Hergert (19) suggested, based on model and isolated lignin studies, the 1660 cm^{-1} absorbance in lignin was attributable to a ketone α to an aromatic ring, with the para-position etherified and with an oxygen atom (as a hydroxyl group or etherified) on the β-carbon atom. An example is shown in Fig. 45.

Coniferaldehyde structures in untreated FW lignin also contribute, though to a lesser extent, to the conjugated carbonyl absorption at 1660 cm^{-1}.

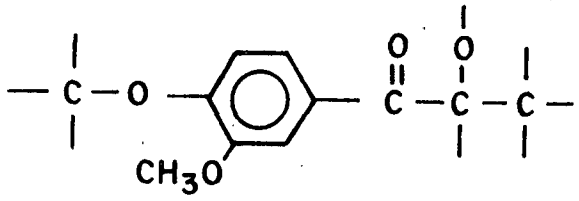

Figure 45. Para-Substituted Aryl Ketone Structure in Lignin (α-carbonyl)

Ozonation of fiberized wood could be expected to generate various other conjugated carbonyl groups in the lignin (see Background under Introduction) that may absorb near 1660 cm^{-1}. Possibilities include ring-conjugated aldehydes and ketones, α,β-unsaturated aldehydes and carboxylic acids, and quinone structures (19,36,67,71).

Table XX shows the conjugated carbonyl absorbance values found for the various FW difference spectra. The values found for total and insoluble carbonyl represent the net difference in conjugated carbonyl content between untreated and ozonated FW samples.

TABLE XX

CONJUGATED CARBONYL ABSORBANCE AT 1660 CM^{-1}

Ozone, %	Total[a] Carbonyl	Insoluble[b] Carbonyl	Water-Soluble[c] Carbonyl	Water-Soluble[d] Carbonyl
1.0	0.000	-0.004	0.004	0.019
3.0	0.041	-0.013	0.054	0.069
5.0	0.037	-0.004	0.041	0.043
7.0	0.035	-0.011	0.046	0.049

[a]From difference spectra of ozonized, unwashed FW minus untreated FW.
[b]From difference spectra of ozonized, washed FW minus untreated FW.
[c]By difference, Total Carbonyl — Insoluble Carbonyl = Water-Soluble carbonyl.
[d]From difference spectra of ozonized unwashed FW minus ozonized, washed FW.

The absorbance value of zero, as found for total carbonyl at 1% ozone consumption, indicated conjugated carbonyl (above the amount initially present in untreated FW) was not detected. Positive absorbance values were found for total carbonyl, at the higher ozonation levels, indicating formation of conjugated carbonyl functionalities had occurred. The extent of conjugated carbonyl formation remained relatively constant, regardless of the ozone consumption level.

The negative absorbance values found for insoluble carbonyl showed there was less conjugated carbonyl present in ozonated FW than in untreated FW. The carbonyl was removed from the FW along with the solubilized lignin it was associated with and/or through ozone modification of the lignin (i.e., loss of aromaticity thereby shifting the carbonyl absorbance to that of unconjugated functionalities).

It was previously found (Table III) that ozonation resulted in solubilization of lignin and it was shown (Table XX) that conjugated carbonyl groups (which should aid lignin solubility) were formed in the lignin of ozonated FW, at the higher ozonation levels. Thus it seemed logical to conclude loss of conjugated carbonyl groups occurred through their concurrent solubilization with the lignin of FW.

The positive absorbance values obtained for water-soluble carbonyl (Table XX) verified that solubilization of conjugated carbonyl functionalities occurred upon ozonation of FW. The agreement between the water-soluble carbonyl absorbance values determined by difference and the values obtained from the difference spectra was quite good.

Aromatic absorbance (1600 and 1510 cm^{-1}) was evident in difference spectra representing the water-soluble fraction of ozonized FW (Appendix VII). The IR spectra of isolated, water-soluble reaction products (Appendix XIV) also gave

evidence for the presence of some aromatic material (absorbance at 1510 cm^{-1}). These results indicated a portion of the aromatic rings in lignin were being solubilized intact. Incorporation of polar functional groups, such as carbonyls, into the aromatic degradation products would be necessary in order to make the aromatic material water soluble.

Balousek (11) and Kojima, et al. (12) each found reaction products with intact aromatic rings following ozonation of lignin model compounds (dimers).

In summary, it was concluded ozonation of FW resulted in generation of conjugated carbonyl groups within the lignin structure. Once sufficient lignin degradation occurred to free lignin fragments from the bulk polymer, these newly introduced carbonyl functionalities, plus those initially present, aided solubilization of the modified lignin material. Some of the lignin material was solubilized with intact aromatic rings.

Mechanisms for Generation and Solubilization of Conjugated Carbonyl Groups in Ozonated FW Lignin

Carbonyl analysis, based on FT-IR difference spectra, showed conjugated carbonyl groups were formed in ozone-treated fiberized wood. Washing of the ozonated FW resulted in solubilization of conjugated carbonyl functionalities.

Several plausible mechanisms illustrating reaction routes for generation of conjugated carbonyl groups in ozonated FW lignin are shown in Fig. 46-49.

The mechanism shown in Fig. 46 is similar to that proposed by Soteland (18) for the ozone oxidation of aromatic rings in lignin.

The mechanism shown in Fig. 47 is based on a mechanism proposed by Singh (6).

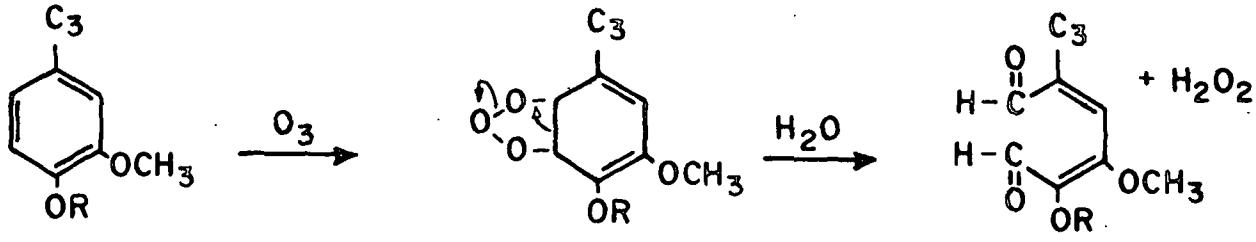

Figure 46. 1,3 Dipolar Addition of Ozone to Aromatic Ring Resulting in Formation of Conjugated Aldehyde Functionalities in Lignin

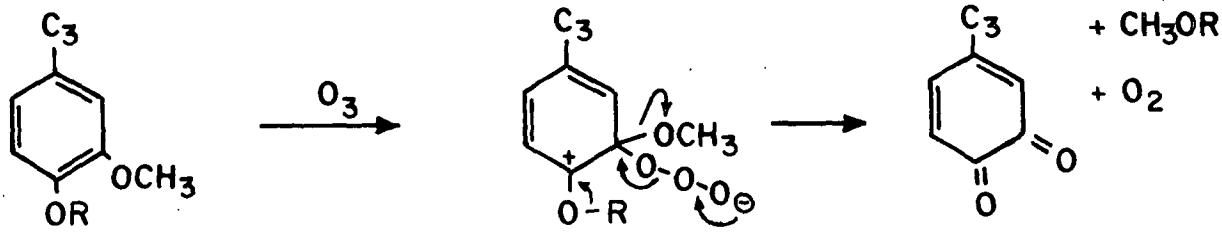

Figure 47. Electrophilic Substitution of Ozone at Aromatic Ring Resulting in Demethoxylation and Quinone Formation in Lignin (6)

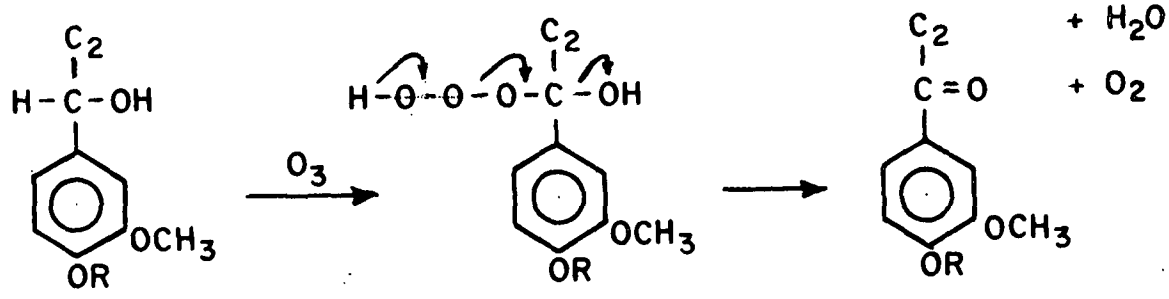

Figure 48. Ozone Insertion at α-Carbon to Form Conjugated α-Carbonyl Group in Lignin

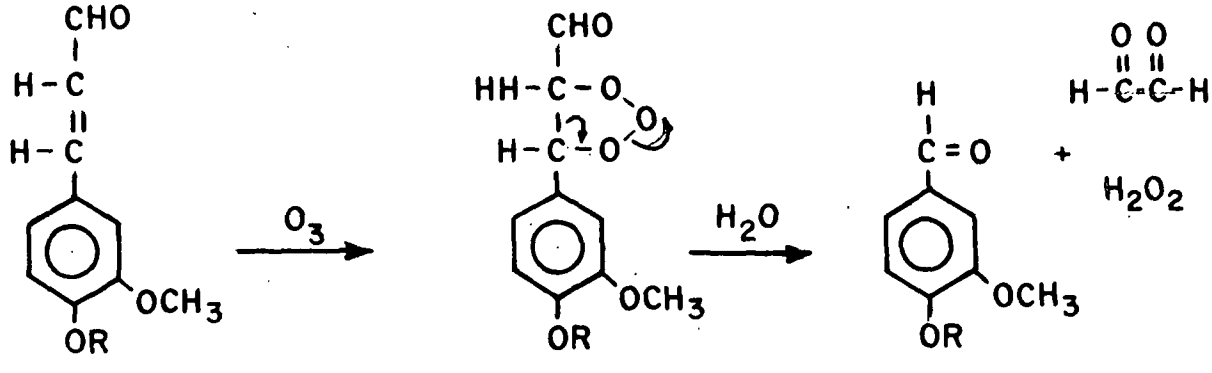

Figure 49. Ozone Degradation of Coniferaldehyde Structure in Lignin via Criegee Mechanism (8) to Form Conjugated Aldehyde

The possible mechanisms for generation of conjugated carbonyl structures in ozonated FW lignin are many and varied. Those shown in Fig. 46-49 are merely examples of the types of reactions that might be occurring in a fiberized wood system.

As previously mentioned, washing of the ozonated FW resulted in solubilization of conjugated carbonyl groups and lignin. This concurrent solubilization might be envisioned as shown in Fig. 50, where cleavage of the ether connecting bonds frees the modified guaiacyl unit from the bulk lignin polymer.

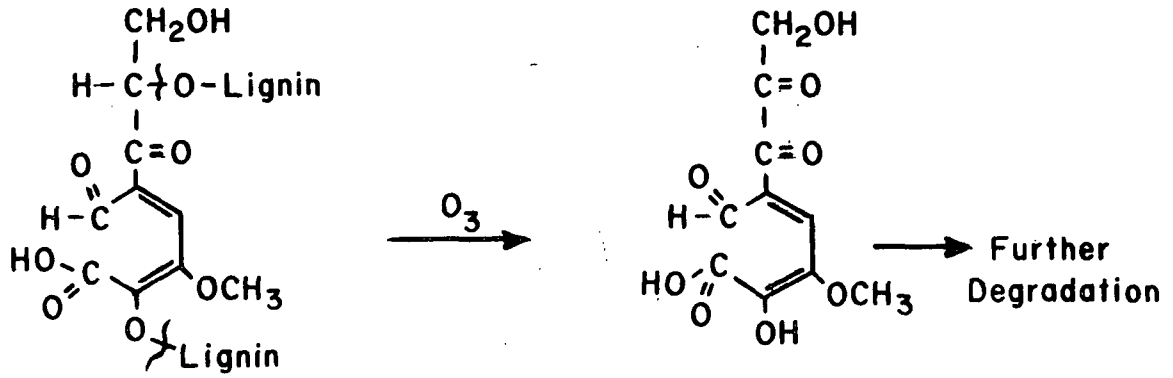

Figure 50. Solubilization of Conjugated Carbonyl Groups in Lignin

Estimate of Decrease in Conjugated, Noncarboxyl Carbonyl Content in Ozonated Fiberized Wood Lignin

The magnitude of the decrease in conjugated, noncarboxyl carbonyl content of ozonated FW lignin was estimated. This was done by comparing absorptivities (at 1660 cm^{-1}) calculated for the untreated and ozonated FW samples. The absorptivities were calculated from normalized spectra of neutralized FW (see Experimental section for normalizing process) and the lignin content of each sample. The results are given in Table XXI.

The absorptivities calculated for ozonated FW were lower than that of untreated FW. This indicated there were fewer conjugated, noncarboxyl carbonyl

groups in the residual lignin of ozonated FW. The decrease in carbonyl content was also found to be greater in the more highly ozonized FW.

TABLE XXI

CONJUGATED, NONCARBOXYL CARBONYL ABSORPTIVITY

Ozone, %	Normalized[a] Absorbance	Lignin, mg[b]	Absorptivity, (absorbance/ mg lignin)
0.0	0.027	0.281	0.096
1.0	0.018	0.269	0.067
3.0	0.013	0.244	0.053
5.0	0.011	0.219	0.050
7.0	0.009	0.201	0.045

[a] At 1660 cm^{-1}, based on normalized spectra of neutralized FW.

[b] Klason + acid-soluble lignin, based on 1-mg sample o.d. FW.

Based on the absorptivities, approximately half as many conjugated, noncarboxyl carbonyl groups were present in 7% ozonized FW lignin as compared to untreated FW lignin.

The 1660 cm^{-1} absorbance represents, in part, the α-carbonyl groups in lignin (19). Adler and Marton (72) estimated there were 7 α-carbonyl and 3 coniferaldehyde groups per 100 lignin C-9 units in spruce Bjorkman lignin, which represented the conjugated, noncarboxyl carbonyl component.

In view of the decreasing absorptivities (Table XXI) found for ozonated FW, it was concluded there were fewer α-carbonyl groups in the residual lignin of ozonated FW as compared to the lignin of untreated FW.

Crozier (53) found peroxyacetic acid oxidation of loblolly pine dioxane lignin also resulted in loss of α-carbonyl groups.

Since it was concluded there were fewer α-carbonyl groups in ozonated FW lignin, there must have been fewer reaction sites (α-carbonyls) in ozone pretreated FW, that was subsequently pulped with oxygen/alkali. Further discussion of this subject is found in the ozone pretreatment section (p. 107).

PHENOLIC HYDROXYL

The importance of the phenolic hydroxyl group as an active delignification site in oxygen/alkali pulping has been discussed in the Background section. Singh (6) and Hatakeyama, et al. (14) both proposed mechanisms whereby ozonation of lignin resulted in formation of phenolic hydroxyl groups.

The accurate determination of free-phenolic hydroxyl groups in isolated lignin is rather difficult (54). Estimating the phenolic hydroxyl content of lignin contained in fiberized wood is even more difficult. No standard methods of analysis have been adopted for wood systems.

The effect of ozone on the phenolic hydroxyl content of lignin in FW was analyzed using FT-IR difference spectroscopy and a selective methylation technique.

Use of FT-IR Difference Spectroscopy for Phenolic Hydroxyl Analysis

Hergert (19) has attributed absorbance at 1220 cm^{-1} to the C-O stretch of the phenolic hydroxyl group, based on infrared studies of conifer lignin and related lignin models. Bellamy (73) assigned the absorbance near 1200 cm^{-1} in phenols to the phenolic hydroxyl group.

The infrared spectra of untreated and ozonated fiberized wood (FW) all showed a characteristic absorbance at 1220 cm^{-1}. This particular absorbance was absent in the spectrum of holocellulose isolated from untreated and ozonated FW (Appendix XVI), suggesting the absorbance arose from lignin rather than carbohydrate. Crozier (53) observed the 1220 cm^{-1} absorbance in the IR spectrum of dioxane lignin isolated from the same loblolly pinewood used in this study (Appendix XVII).

Based on the above evidence, the IR absorbance at 1220 cm^{-1} for FW was assigned to the phenolic hydroxyl group.

The neutralized FW difference spectra (Appendix VIII) were used in conjunction with the untreated, neutralized FW transmission spectrum (Appendix V) to obtain a normalized spectrum for absorbance at 1220 cm^{-1}. The phenolic hydroxyl absorbance values obtained using this procedure are given in Table XXII. Neutralized FW spectra were used rather than conventional spectra, since it appeared they were balanced more accurately, thus providing more consistent results for the PhOH analysis.

TABLE XXII

PHENOLIC HYDROXYL ABSORBANCE AT 1220 CM^{-1}
FOR UNTREATED AND OZONATED FIBERIZED WOOD

Ozone, %	Transmission Spectrum	Difference Spectrum	Normalized[a] Spectrum
0.0	0.036	-	0.036
1.0	-	-0.007	0.029
3.0	-	-0.016	0.020
5.0	-	-0.025	0.011
7.0	-	-0.035	0.001

[a]Normalized spectrum = 0.036 + difference spectrum absorbance.

The absorbance values found for the normalized spectra indicated a significant loss of phenolic hydroxyl groups occurred for ozonated FW. The losses were greater at the higher ozonation levels.

The decreases in phenolic hydroxyl content reflect losses associated with solubilized lignin and any *in situ* losses caused by ozone modification of the lignin in FW.

Methylation Technique for Estimate of Phenolic Hydroxyl Content in Fiberized Wood

A selective methylation technique was used to estimate the phenolic hydroxyl content of untreated and ozonated FW. The technique was similar to that developed by Andrews and Des Rosiers (74), who methylated jack pine groundwood with dimethyl sulfate and 30% NaOH, under controlled pH ($\approx$ 9.0) and a nitrogen atmosphere. They measured small increases in methoxyl content which they attributed to methylation of only the free phenolic hydroxyl groups in the lignin component. This hypothesis was supported by further reaction studies which included identification of free-phenolic groups through selective oxidation with potassium nitrosodisulfonate.

Johnson (5) methylated alkali-fiberized loblolly pinewood under the mild, controlled conditions used by Andrews and Des Rosiers (74). He found subsequent oxygen/alkali delignification of the methylated wood to be substantially inhibited. The reduced delignification was attributed to a significant reduction in concentration of phenolate anion intermediates (due to loss of free-phenolic hydroxyl groups through methylation), which assumed a key role in oxygen/alkali delignification.

Methylation of Untreated Fiberized Wood

The untreated FW was methylated under the controlled conditions employed by Andrews and Des Rosiers (74), and later by Johnson (5). The average methylation pH was varied between 9.0 and 12.5 (details of the methylation technique are given in the Experimental section). The methylation results for untreated FW are given in Table XXIII, where they are listed in order of decreasing average pH. The initial methoxyl content of untreated FW was 4.85%.

TABLE XXIII

METHYLATION OF UNTREATED FIBERIZED WOOD
EFFECT OF pH ON METHYLATED YIELD AND FINAL METHOXYL CONTENT

Av. pH[a]	Yield, %[b]	Methoxyl, %	Increase, %[c]
12.8	100.7	6.16	27
12.4	100.3	6.30	30
11.5	99.4	6.19	28
11.4	99.4	5.94	22
11.2	99.8	5.99	24
11.2	99.2	5.98	23
11.1	99.4	5.95	23
10.9	98.4	6.03	24
10.7	98.5	5.97	23
10.4	98.3	5.83	20
10.3	99.0	5.83	20
10.1	99.1	5.79	19
10.0	100.1	5.69	17
9.7[d]	100.0	5.60	15
9.0[e]	99.2	5.18	7

[a] pH controlled with 15% NaOH.
[b] Based on untreated o.d. fiberized wood.
[c] Based on initial methoxyl content of 4.85% for untreated FW.
[d] pH controlled with 5% NaOH.
[e] pH controlled with 1% NaOH.

The methylation of untreated FW was found to be very pH dependent. High pH (>11.4) gave methoxyl increases of 27-30%, while lower pH (9.0) gave an increase of only 7%. Methylated yields ranged from 98.3-100.7% indicating only

small amounts of FW were being solubilized under the alkaline methylation conditions. Methylation results were very reproducible as shown by the two experiments run at pH = 11.2, where final methoxyl contents differed by only 0.01%.

Andrews and Des Rosiers (74) controlled methylation pH at approximately 9.0 and found the methoxyl content of jack pine groundwood increased about 25%. Johnson (5) methylated alkali-fiberized loblolly pine near pH 9.0 and observed a 28% increase in methoxyl content. In this study, methylation of FW at pH 9.0 resulted in only a 7% increase in methoxyl content. A pH in the range of 11.2-11.5 was necessary to obtain a 25% increase in methoxyl content for untreated FW.

A few subtle differences in reaction conditions were the only obvious reasons for the discrepancies between the results of this methylation work and the results of the two previously mentioned studies (5,74). The methylation apparatus (see Experimental section) used in this study was significantly smaller in size than those described in the literature. Johnson (5) was working with 60 g o.d. fiberized wood samples at 3% consistency, and controlling pH with 30% NaOH. In this study, 1 g o.d. FW samples at 1% consistency were used, and the pH was controlled with 15% NaOH. The FW was also used in Wiley milled form (to pass a No. 80 mesh screen), rather than in fiberized form.

It is possible the larger sample sizes used in previous methylation studies (5,45) provided a greater buffering effect, thus permitting effective pH control near 9.0, even though the total alkalinity of the systems was substantially higher.

The pH of a solution, especially a FW slurry, is not necessarily a good indication of the local acidity or alkalinity of the solution. It is also possible pH measurement is more difficult (less accurate) in a 3% consistency slurry made of coarse wood fibers as compared to a 1% consistency slurry of Wiley

milled FW. At higher consistency mixing might be slower and, temporarily, higher pH might exist in the vicinity of hydroxide addition. This could result in more methylation. It would seem the use of Wiley milled wood at lower consistency rather than fiberized wood at higher consistency, should facilitate establishment of equilibrium between the solid and solution. Thus pH should be a fairly accurate indication of the percent ionized hydroxyl groups in the solution.

In this study, effective pH control was only possible at pH = 10.0 or higher. Once the pH was allowed to fall below about 10.0, a rapid pH drop ensued and compensation with sodium hydroxide to a particular pH level was rather difficult. The most effective pH control was obtained at pH $\geq$ 10.8. In these methylation experiments, pH could be controlled within about 0.1 pH unit.

Based on the methylation results given in Table XXIII, a plot of methoxyl content versus average methylation pH was made for untreated FW. The plot is shown in Fig. 51.

There was a fairly constant increase in methoxyl content as the methylation pH was increased from 9.0 to 12.8. Rydholm (75) estimated pKa values of 10.5-11.0 for the phenolic hydroxyl groups in lignin. Based on this estimation and the fact that effective pH control was possible near 11.0, methylation experiments used to estimate the phenolic hydroxyl content of untreated and ozonated FW were carried out at a pH of 11.1.

Validity of the Methylation Technique for Estimating Phenolic Hydroxyl Content of Fiberized Wood

The validity of the methylation technique depended upon how selectively the phenolic hydroxyl groups were methylated in comparison to the other hydroxyl (aliphatic and enolic) groups present in FW.

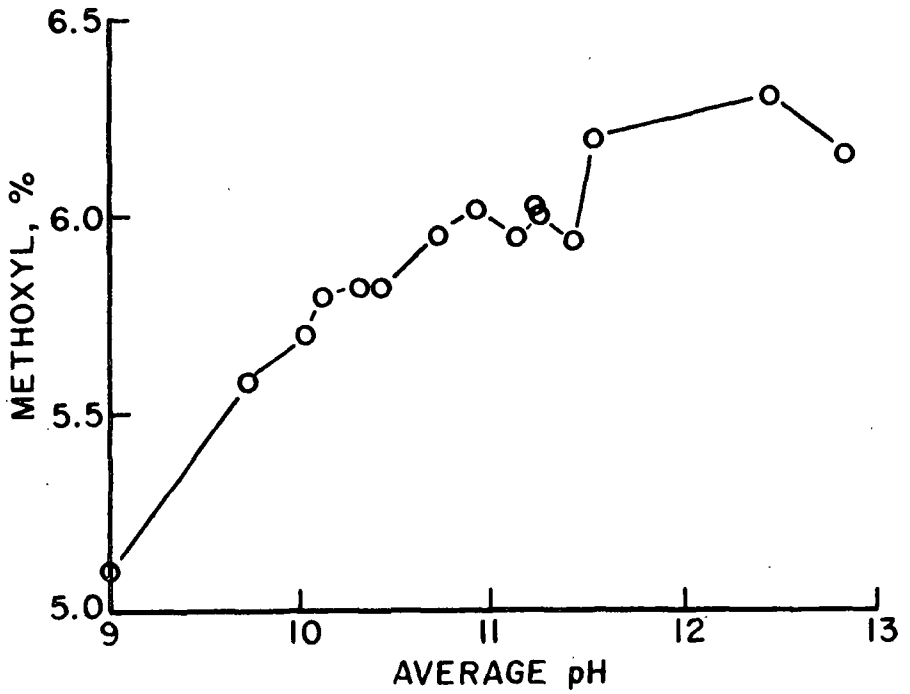

Figure 51. Methoxyl Content versus Methylation pH for Untreated Fiberized Wood

Ionization of phenolic hydroxyls is a necessary prerequisite for methylation with dimethyl sulfate. The pKa values of enolic and aliphatic hydroxyl groups are higher than those of phenolic hydroxyl groups (76). The pKa's of aliphatic hydroxyl groups in cellulose were estimated to be approximately 14.0 (77). Thus at pH 11, the aliphatic and enolic hydroxyls were probably not ionized to the same degree as phenolic hydroxyls and, therefore, were methylated to only a limited extent.

An experiment was performed to test the ease with which pure cellulose could be methylated. A Wiley milled sample of cotton linters (Hercules PS-57) was methylated at pH = 11.1, under the same conditions used for FW methylation. The initial methoxyl content was 0.25% and the final methoxyl content 0.57%. It was concluded cellulose was rather difficult to methylate at the conditions used for FW methylation. This finding substantiates the hypothesis that alipha-

tic hydroxyl groups were not ionized, and subsequently methylated, to a significant degree near pH 11.

Cellulose obtained by chemical treatment of cotton linters would be more accessible to chemical reagents than native cellulose as it exists in FW. Therefore, one could safely predict the native cellulose in FW was at least as difficult to methylate as cotton linters.

The previous methylation results (Table XXIII and Fig. 51) indicated, even at the highest pH levels (11.5-12.8), only a limited amount of methylation (27-30% methoxyl increase) occurred in untreated FW.

This limiting effect was substantiated by two experiments in which previously methylated FW (methoxyl content = 6.02%) was remethylated at pH 10.5 and 11.2. The remethylated FW showed increases in methoxyl content of only 3-4% and had total methoxyl contents (after both methylations), which corresponded to increases of 27-29%. These values compared favorably with the upper limit of 30% methoxyl increase found at pH = 12.4. Thus it was concluded methoxyl contents were approaching maximum values after which further methylation of the FW was rather difficult.

Methylation of Ozonated Fiberized Wood

Ozonated FW was methylated with dimethyl sulfate under the controlled conditions used by Andrews and Des Rosiers (74) (see Experimental section). The pH was controlled at 11.1.

The methylation results for ozonated FW are given in Table XIV, along with the previously obtained result for untreated FW wood methylated at pH 11.1.

The methylated yield for untreated FW approached 100%, but values for ozonated FW indicated some solubilization of wood components occurred under the

alkaline reaction conditions. Soteland (2) found alkali treatment (0.1N NaOH) of ozonized western hemlock groundwood resulted in drastic loss of yield. He concluded ozonation caused substantial modification of the lignin rendering it alkali soluble.

Interpretation of methylation results was based on the assumption that the material solubilized under the alkaline reaction conditions was lignin, and the phenolic hydroxyl content of this alkali soluble lignin was the same as the phenolic hydroxyl content of the lignin in FW.

The 22.7% increase in methoxyl content found for untreated FW compares favorably with results of previous methylation studies performed under similar conditions. Andrews and Des Rosiers (74) found a 25% methoxyl increase for jack pine groundwood, while Johnson (5) obtained a 28% increase for alkali-fiberized loblolly pine.

Methoxyl increases (Table XXIV) found for both untreated and ozonated FW varied from 19.5-24.1%. Increases in methoxyl content were attributed primarily to the methylation of phenolic hydroxyl groups in fiberized wood. Similar increases for both untreated and ozonated FW were, therefore, indicative of similar phenolic hydroxyl contents.

The values obtained for the ratio of final methoxyl content minus initial methoxyl content divided by residual lignin content (Table XXIV), also showed small and seemingly inconsistent variation. This again suggested ozonation had only a small effect, if any, on the phenolic hydroxyl content of the *in situ* lignin in fiberized wood.

TABLE XXIV

SELECTIVE METHYLATION OF UNTREATED AND OZONATED FIBERIZED WOOD[a]

Ozone, %	Methylated Yield, %	Methoxyl Content, %		Increase, %	$M_f - M_i$/, Lignin Content[b]
		Initial	Final		
0.0	99.2	4.85	5.95	22.7	0.039
1.0	97.0	4.58	5.48	19.7	0.034
3.0	91.9	3.91	4.82	23.3	0.040
5.0	93.8	3.64	4.35	19.5	0.036
7.0	93.5	3.03	3.76	24.1	0.042

[a]All values based on untreated o.d. FW (i. e., corrected for ozonated yield) methylation pH = 11.1.

[b]Ratio of final methoxyl content minus initial methoxyl content divided by residual lignin content (Klason + acid-soluble) of FW.

Calculation of Phenolic Hydroxyl Content in Untreated and Ozonated Fiberized Wood Based on Methylation Results

The phenolic hydroxyl content of untreated and ozonated FW was calculated. The initial and final methoxyl contents (Table XXIV) found for untreated and ozonated FW, before and after selective methylation, were used to estimate the phenolic hydroxyl content.

It was assumed untreated FW lignin had a methoxyl content of 16%, and that 93% of the methoxyl present in untreated and ozonated FW was associated with the lignin. It was also assumed that α-cellulose (cotton linters) methylates to approximately the same extent as the holocellulose in FW. All phenolic hydroxyl contents were corrected, based on the above assumption, according to the calculated amount of holocellulose present in the FW samples and the methylation result found for cotton linters (see Appendix XVIII).

The phenolic hydroxyl contents determined for untreated and ozonated FW are given in Table XXV.

TABLE XXV

PHENOLIC HYDROXYL CONTENT OF FIBERIZED WOOD BASED ON SELECTIVE METHYLATION AT pH = 11.1

Ozone, %	Phenolic Hydroxyl, (#/100 C-9 units)
0.0	19
1.0	15
3.0	18
5.0	14
7.0	17

Adler, et al. (78) found 20-25 phenolic hydroxyls per 100 lignin C-9 units in spruce Bjorkman lignin, using a periodate oxidation method. However, he concluded there were probably less than 20 PhOH/100 C-9's in unaltered (in situ) spruce lignin, since it was shown (79,80) vibratory ball-milling procedures used to isolate Bjorkman lignin caused some liberation of phenolic hydroxyl groups. Thus, the value of 19 PhOH/100 C-9's found in this study for untreated FW seems reasonable.

The phenolic hydroxyl contents of ozonated FW were all found to be slightly lower than the value obtained for untreated fiberized wood. It was, therefore, concluded that ozonation of fiberized wood resulted in a slight decrease in the phenolic hydroxyl content of the residual lignin in ozonated FW.

Hatakeyama, et al. (14) found a decrease in phenolic hydroxyl content for ozonated calcium lignosulfonate. Crozier (53) observed only slight increases

(i.e., 5% or less) in phenolic hydroxyl content for loblolly pine dioxane lignin oxidized with peroxyacetic acid.

The loss of free phenolic hydroxyl groups through ozonation is not desirable from the standpoint of ozone pretreatment of FW for oxygen/alkali pulping, since phenolic hydroxyls are postulated reaction sites in oxygen/alkali delignification (32,33). Further discussion of phenolic hydroxyl groups in relation to ozone pretreatment is included in a later section.

Proposed Mechanism for in situ Loss of Phenolic Hydroxyl Groups in FW Lignin

A possible mechanism, similar to that proposed by Singh (6), for in situ loss of phenolic hydroxyl groups, is shown in Fig. 52.

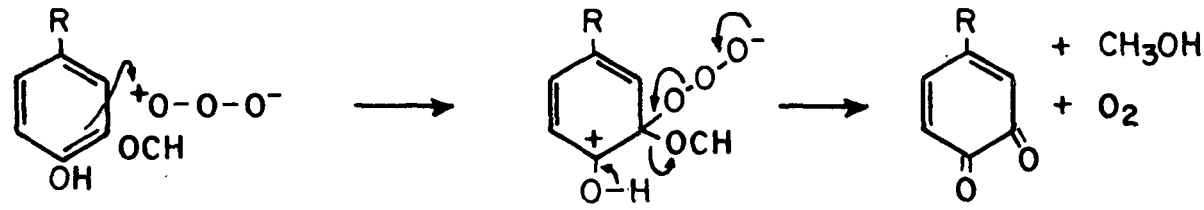

Figure 52. Ozonation of Lignin Resulting in Loss of Phenolic Hydroxyl Group

Kojima, et al. (12) proposed the formation of phenoxy radicals in ozonized softwood lignin model compounds. Free-radical reactions could be envisioned as modifying phenolic hydroxyl groups in lignin as shown in Fig. 53.

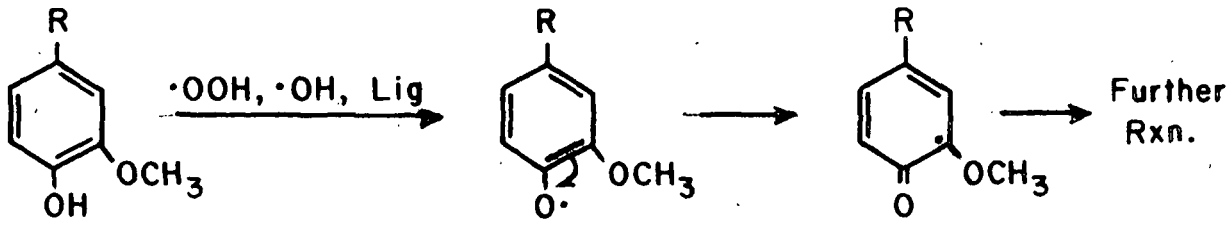

Figure 53. Free-Radical Oxidation of Phenolic Hydroxyl Group in Lignin

ACTIVE OXYGEN

Active oxygen is considered capable of separating iodine from a KI solution in acidic medium. The oxygen can be bound as hydroperoxide, peroxide, ozonide or quinonoid functional groups (13).

Katuscak, et al. (13,15-17), in studies on isolated methanol and HCl lignins, showed ozonation of these insoluble lignins produced active oxygen functional groups (see Background under Introduction). Soteland (2,4,18) detected active oxygen in ozonated groundwood and thermomechanical pulps.

The active oxygen contents of freshly ozonized FW were measured in this study (see Experimental section for details of analytical procedure). The results are given in Table XXVI.

TABLE XXVI

ACTIVE OXYGEN CONTENT OF OZONATED FIBERIZED WOOD

Ozone, %	Active Oxygen, % as H_2O_2[a]	
	This Work	Literature[b]
1.0	0.1	0.2
3.0	0.3	0.4
5.0	0.5	-
7.0	0.4	-

[a]Percentage based on o.d. ozonized FW.

[b]Obtained by Soteland (2) for thermomechanical pulp.

Active oxygen was generated upon ozonation of FW. The concentration of active oxygen functionalities (hydroperoxides, peroxides, ozonides, quinones) increased in the more highly ozonized FW.

The active oxygen contents determined for ozonated FW represented only the water-soluble portion of these functionalities. Therefore, the values obtained only served as rough estimates of the minimum amount of active oxygen produced by ozonation of FW. It is likely insoluble active oxygen groups, that went undetected as a consequence of the analysis procedure, were also present in ozonated FW.

Mechanisms for Active Oxygen Formation in Ozonated Fiberized Wood

Plausible mechanisms for the formation of active oxygen groups in FW lignin, and subsequent secondary reactions leading to their destruction and/or conversion to other types of active oxygen functionalities, are shown in Fig. 54 and 55.

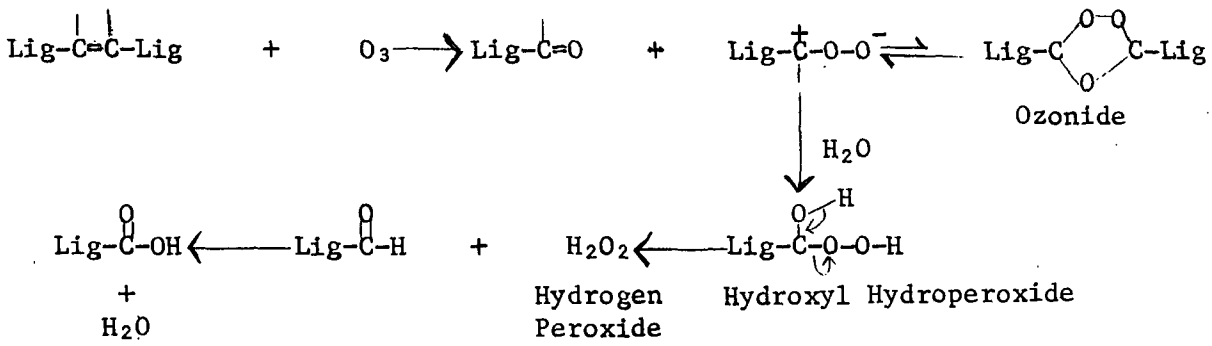

Figure 54. Formation of Active Oxygen Functional Groups in Lignin

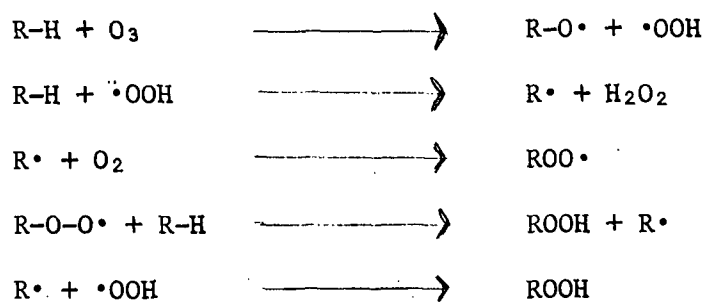

Figure 55. Free-Radical Mechanism for Generation of Active Oxygen Functional Groups in Ozonated Fiberized Wood

Reaction of the olefinic or aromatic bonds in lignin by a mechanism analagous to that proposed by Criegee (8) can account for the production of the active oxygen groups labeled above. The reaction of the zwitterion fragment, with methanol produced during ozonolysis, is also a possibility. This would result in the formation of a methoxy hydroperoxide, whose decomposition would lead to the formation of methyl peroxide.

Ozone-initiated free-radical reactions serve as another possible route for production of active oxygen functional groups in ozonated FW. The free-radical reactions are nonspecific, thus lignin and carbohydrate components may both be involved. However, Katuscak, et al. (13,16,17) found the aromatic conjugated system and the polymeric matrix of the lignin macromolecule had a stabilizing influence on free-radicals formed in ozonized lignin. This stabilizing effect may aid the propagation of free-radicals in lignin.

A free-radical mechanism for generation of active oxygen functional groups in ozonated FW is shown in Fig. 55. The mechanism is similar to that proposed by Katuscak, et al. (17) for generation of active oxygen functionalities in ozonized lignin.

The reactions shown in Fig. 55 provide a mechanism for generation of both hydroperoxide and hydrogen peroxide, each of which could be detected as active oxygen.

ESTER AND LACTONE

Soteland (18) suggested the possibility of ester and lactone formation in the ozonation of western hemlock groundwood. Balousek (11) and Kojima, et al. (12) both isolated lactones and esters in their studies involving ozonation of lignin model compounds (see Introduction, Background).

There was a small amount of evidence found in this study that suggested the possibility of ester and/or lactone formation in the reaction of fiberized wood with ozone.

The maximum unconjugated carbonyl absorbance characteristically occurred near 1730 cm^{-1} in the majority of the FT-IR difference spectra. However, an upward shift in this maximum absorbance to 1750-1760 cm^{-1} was observed for the ozonized, washed FW minus untreated FW difference spectra (Appendix VII) at ozone consumption levels of 1 and 3%.

This absorbance shift may merely be an artifact of the nulling process used to obtain the difference spectra. Another possibility is ester and lactone formation, which is known to raise the carbonyl frequency significantly above that of normal ketones and aldehydes by the influence of the adjoining oxygen atom (67,71).

The fact that the absorbance shift only occurred at the lower ozone levels (1 and 3%) could be explained in terms of muconic acid rearrangement. Muconic acid derivatives would be expected in the highest concentrations in FW treated with minimal amounts of ozone, since they contain olefinic bonds which are very susceptible to further oxidation by ozone.

The rearrangement of muconic acid derivatives to the corresponding lactone is likely based on the results of lignin model studies (9,11,12,81). The α,β-unsaturated lactones formed by the rearrangement absorb in the infrared in the appropriate range (1740-1760 cm^{-1}) for the absorbance shift (71).

SUMMARY — EFFECT OF OZONE OXIDATION ON SPECIFIC FUNCTIONAL GROUPS IN FIBERIZED WOOD

Methoxyl

Ozonation of fiberized wood resulted in solubilization of methoxyl groups. It appeared one methoxyl group was solubilized along with each C-9 lignin unit solubilized. Approximately 70% of the methoxyl solubilized by ozone treatment was lost as volatile components, possibly methyl esters or methanol. There was no *in situ* modification of the methoxyl groups present in the residual lignin of ozonated FW.

Carboxyl

Large amounts of carboxyl groups (up to 106 meq/100 g o.d. FW) were formed upon ozonation of fiberized wood. The majority of these functionalities (63-97%) were water-soluble and removed from the fiberized wood during the washing process. Oxalic acid represented 10% of the total water-soluble material at the 5% ozone level. Ozonated, washed FW had 20-50% more carboxyl than untreated fiberized wood.

A linear relationship existed between carboxyl produced and ozone consumed. It was found that 70-78% of the ozone consumed by FW ends up as carboxyl, except at the 1% ozone level.

Unconjugated Carbonyl

Unconjugated carbonyl groups were formed during ozonation of FW. Their formation was associated primarily with lignin, but some carbohydrate involvement was also likely. Increasing amounts of unconjugated carbonyl were formed as ozone consumption levels were increased. A trend toward increasing water solubility was also observed.

Both noncarboxyl and carboxyl carbonyl were produced in the ozonation of FW. Carboxyl carbonyl was discussed previously. In situ, noncarboxyl carbonyl formation was limited to ketone, ester, and/or aldehyde groups on the β- and γ-carbons of the lignin side chains. It may have also been represented by ketone, lactone, or aldehyde formation in the holocellulose component.

It was estimated a maximum of 2-4 times more unconjugated, noncarboxyl carbonyl was present in the residual lignin of ozonated FW as compared to the lignin of untreated FW.

Conjugated Carbonyl

Conjugated carbonyl groups were formed and solubilized during ozonation of fiberized wood. Their formation was associated only with lignin. Ozonation also resulted in modification and subsequent solubilization of conjugated carbonyl that was initially present in untreated FW lignin. Some of the water-soluble conjugated carbonyl was associated with intact aromatic rings.

There were approximately half as many conjugated, noncarboxyl carbonyl groups in 7% ozonized FW lignin as in untreated FW lignin. It was concluded loss of conjugated carbonyl groups occurred through their concurrent solubilization with the lignin of fiberized wood.

Phenolic Hydroxyl

The phenolic hydroxyl content of ozonated FW was found to be slightly lower than that of untreated FW. The selective methylation technique seemed to give reasonable values for phenolic hydroxyl content of FW.

Active Oxygen

Small amounts (maximum of 0.5% as H_2O_2) of active oxygen were detectable in freshly ozonized FW. This represented the formation of hydroperoxide, ozonide, peroxide, and/or quinone functionalities. Formation of these groups in ozonated FW appeared feasible via ionic and free-radical mechanisms.

OZONE OXIDATION OF FIBERIZED WOOD — AS A PRETREATMENT FOR OXYGEN/ALKALI PULPING

The ozone pretreatment work of Johnson and McKelvey (5) was reviewed in the Background section (Introduction). These researchers found ozone pretreatment of alkali-fiberized red maple, prior to oxygen/alkali pulping, resulted in a more selective delignification with less carbohydrate and chain degradation.

In similar oxygen/alkali pulping experiments performed with alkali-fiberized loblolly pine, Johnson and McKelvey (5) found only marginal benefits from the ozone pretreatment. In some experiments a more selective delignification was evident, but in all cases polysaccharide chain degradation was severe.

Some of the results found in this study were applied to Johnson and McKelvey's (5) work in an effort to explain their "marginal" pretreatment results for loblolly pine.

Since Johnson and McKelvey (5) had not chemically characterized the FW, before and after ozone treatment, they did not know to what extent the *in situ* lignin had been modified or exactly how much lignin had been solubilized during washing.

In this study it was estimated a maximum of 9% of the aromatic rings in FW were modified at the 1% ozone treatment level and possibly 20% were modified

at 7% ozone consumption. Since Johnson and McKelvey (5) were working with ozone consumptions of 2.4 % or less, they were probably modifying the *in situ* lignin to only a small extent.

The ozone pretreatment would seem to have had a greater chance for success if larger amounts of *in situ* lignin were chemically modified. This could be done by increasing the ozone dosage.

Kratzl and coworkers (32,33) suggested the importance of free-phenolic hydroxyl groups in the oxygen/alkali delignification of wood. This study indicated a slight decrease in phenolic hydroxyl content for ozonated FW. Thus oxygen/alkali delignification of ozonated FW may be hindered by loss of phenolic hydroxyl reaction sites.

Aoyagi, *et al.* (34) proposed that α-carbonyl groups in lignin were important reaction sites with respect to oxygen/alkali delignification of wood. Based on the results found for this study, it was concluded there were fewer α-carbonyl groups in ozonized FW lignin than in untreated FW lignin. Therefore, ozone pretreatment of FW would not be expected to enhance lignin reactivity in subsequent oxygen/alkali delignification.

Kratzl, *et al.* (32,33) found electron-withdrawing groups such as carboxyl and carbonyl increased the critical oxidation potential of phenolic compounds (made them more difficult to oxidize), while electron-releasing groups, such as methoxyl, had the opposite effect.

The methoxyl content of ozonized FW lignin was found to remain relatively constant ($\approx$ 16%) at about the same level as in untreated FW lignin. Thus, the reaction of ozonized FW lignin in oxygen/alkali could not have been enhanced by

the presence of greater amounts of electron-releasing groups (methoxyl), which would have lowered the critical oxidation potential of the lignin.

In conclusion, ozone pretreatment of alkali-fiberized loblolly pine should have no beneficial effect on subsequent oxygen/alkali delignification of FW. This conclusion is supported by the experimental results of Johnson and McKelvey (5) for ozone pretreated, oxygen/alkali delignified loblolly pine FW, but not for red maple.

CONCLUSIONS

Ozonation has a small modifying effect on the *in situ* lignin of fiberized wood. The majority of the lignin that reacts with ozone is degraded to water-soluble products containing carboxyl and carbonyl functionalities.

The carbohydrate component of fiberized wood undergoes only slight degradation, and subsequent solubilization, upon ozone treatment.

EXPERIMENTAL

PREPARATION OF STARTING MATERIAL

A flow chart illustrating the steps taken to prepare the starting material is shown in Fig. 56. An alkali-fiberized (sodium carbonate-bicarbonate) loblolly pinewood was made at the Bauer Brothers thermomechanical pulp pilot plant in Springfield, Ohio. The fiberization involved wood chip impregnation with alkali, preheating to fiberization temperature, and fiberization with wide plate clearance. The impregnation conditions used in preparation of the FW were as follows (Table XXVII).

Following impregnation, the alkali was drained off leaving the wood chips at approximately 40% consistency. The alkali-impregnated chips were presteamed for 6 min, at 80 psig, to a temperature of 160°C. The heated chips were then fiberized in a No. 418 Bauer, double-disk, pressurized refiner at the conditions outlined below (Table XXVIII).

After fiberization the wood was throughly washed in warm water, dewatered, shipped to the Institute, and stored in the cold room (40°C).

FIBERIZED WOOD YIELD DETERMINATION

Fiberized wood yield could not be determined from the Bauer Brothers process since the experimental runs were not of sufficient duration. Thus, the fiberization process was simulated in the Institute pulp lab using similar reaction conditions and apparatus.

An Asplund mill was operated under steam pressure and the wood discharged directly into a Sprout-Waldron disk refiner run at atmospheric pressure. The yield of alkali-fiberized loblolly pine, following fiberization and washing, was 91.6%.

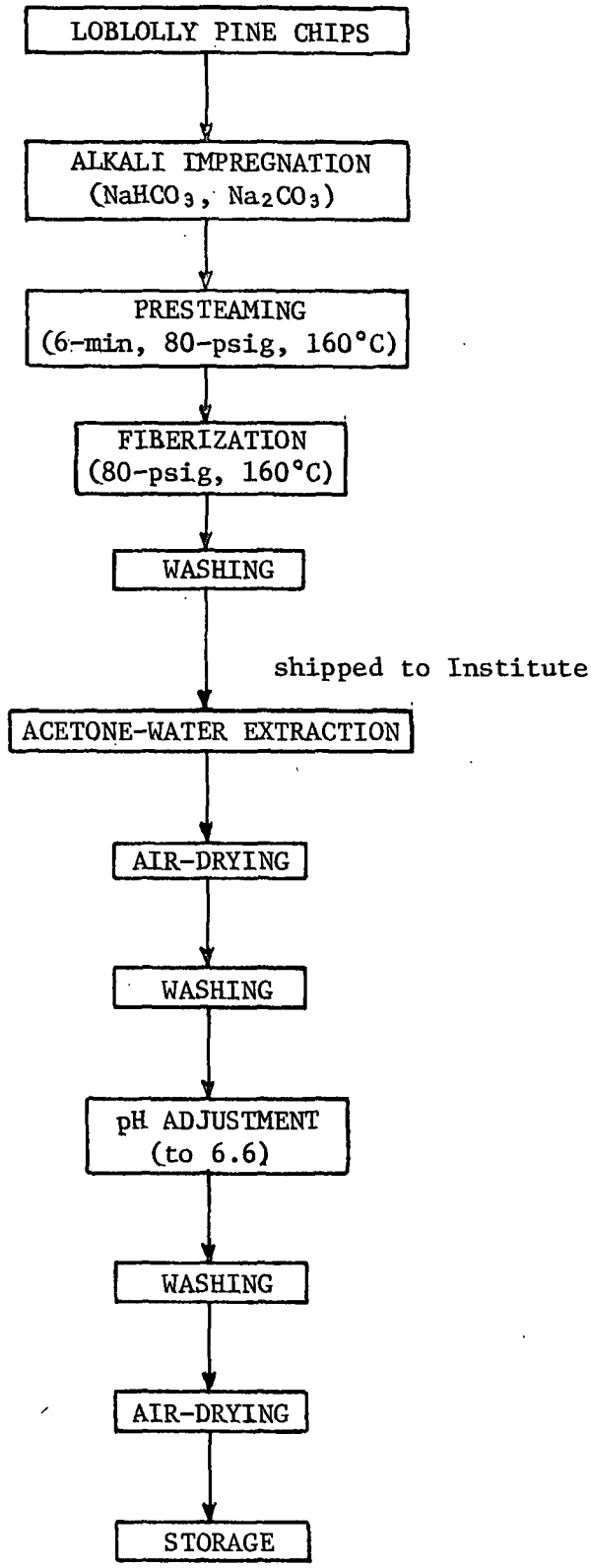

Figure 56. Flow Chart for Preparation of Starting Material

TABLE XXVII

ALKALI-IMPREGNATION CONDITIONS

Na_2CO_3 (% o.d. wood) - 8.8	Consistency (%) - 10
$NaHCO_3$ (% o.d. wood) - 6.7	Temperature (°C) - 92
Time (min) - 30	Air pressure applied (psig) - 100

TABLE XXVIII

REACTION CONDITIONS FOR ALKALI-FIBERIZATION OF LOBLOLLY PINE

Temperature (°C) - 160	Feed rate (ADT/day) - 9.9
Steam pressure (psig) - 80	Line load (HPD/ADT) - 0.9
Plate clearance (inch) - 0.025	

ACETONE-EXTRACTION OF FIBERIZED WOOD

A total of 910 g o.d. FW was extracted for 48 hr in a large Soxhlet apparatus, using a 9:1 acetone-water mixture. The extractive content (see Appendix III) of the FW was determined by distilling off the majority of the solvent and evaporating the extractives, and remaining solvent, to dryness.

Following extraction, the FW was air-dried for 2 days to allow evaporation of any remaining acetone. The fiberized wood was then washed 3 times in hot, deionized water.

pH ADJUSTMENT OF EXTRACTED, FIBERIZED WOOD

The pH of the fiberized wood was adjusted from 8.7 to a neutral value of 6.6 by soaking the wood in dilute HCl ($\approx$ 1 x 10^{-6} N) for 3 hr at room temperature. The FW was then rewashed with hot, deionized water, air-dried for 2 days to a consistency of 90%, and stored in plastic bags away from light.

EXPERIMENTAL APPARATUS

The apparatus constructed for treatment of FW with ozone is shown in Fig. 57. The ozone generator used in this study was a Welsbach Laboratory Ozonator, Model T-816.

The ozone from the main gas stream flowed via glass tubing to a 5-liter reaction flask which was attached to a Buchi Model R evaporator. The evaporator motor rotated the flask to provide uniform gas contact with the fiberized wood surface.

The ozone-oxygen exit gases flowed through a series of two, 500 mL gas washing bottles each filled with 500 mL of a 5% KI solution. An identical set-up was used for gases flowing from the sample line.

The main gas line and sample line were each connected to 3-way stopcocks so the gas streams could be diverted from the reactor and sample line ozone traps into a large ozone trap, prior to the start, and at the end of each reaction.

CALIBRATION OF OZONE GENERATOR

Duplicate runs to determine ozone production and actual line-split ratios for the ozone generator were performed at the reaction conditions given in Table XXIX.

PROCEDURE FOR CALIBRATION OF OZONE GENERATOR

Prior to the calibrations runs, the ozone generator was purged for 45 min with oxygen to remove any residual ozone that might have been present. Two, 500 mL gas-washing bottles were then connected in series to both the sample line and the ozone line of the generator, leaving the 3-way stopcock systems intact

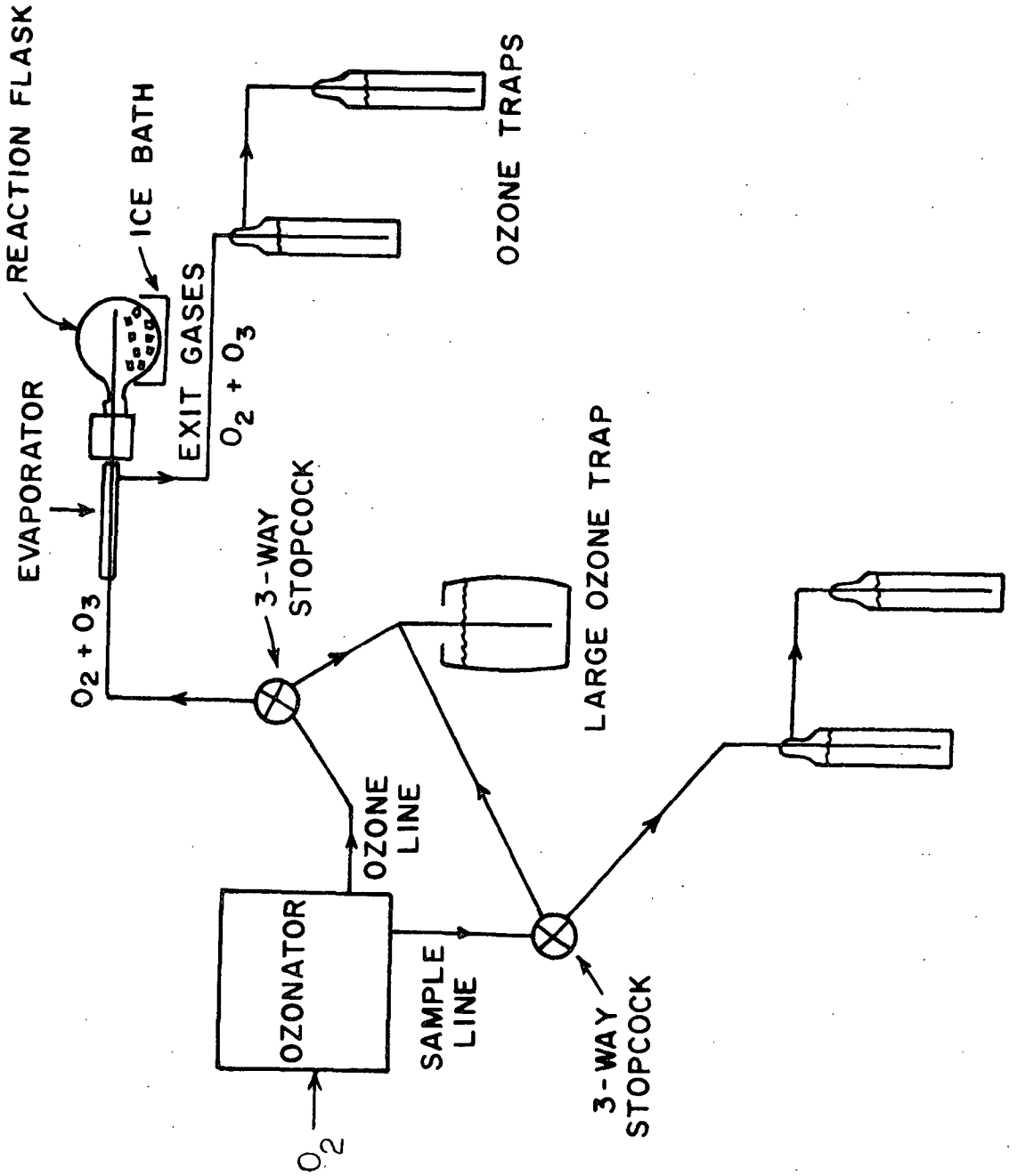

Figure 57. Schematic of Apparatus for Ozonation of Fiberized Wood

(see Fig. 57). The oxygen flows were diverted (by way of the stopcock system) to the large ozone trap and the ozonator power turned on.

TABLE XXIX

REACTION CONDITIONS FOR CALIBRATION OF OZONE GENERATOR

Time (min) - 15	Temperature (°C) - 25
Ozonator pressure (psig) - 8.0	Ozone line flow (liter/min) - 3
Corona discharge power (v) - 120	Sample line flow (liter/min) - 1

The ozone-oxygen gas flows remained diverted for 2 min and were then switched back to the ozone traps (gas-washing bottles) at the start of the calibration run.

At the end of the run, the gas flows were again diverted and the ozone traps removed. The ozone concentration was determined and the ozone production and sample line/ozone line split ratio calculated. The ozone production rate was found to be 0.216 g/min and the split ratio, 3.66.

PREPARATION OF FIBERIZED WOOD FOR OZONE TREATMENT

The air-dry FW was mixed with enough deionized water to obtain a consistency of 3-4%. The FW was allowed to soak in the water for several hours with occasional stirring. The FW slurry was dewatered on a centrifuge for 5 min and then transferred to a pulp fluffing apparatus.

The apparatus consisted of a Lightning mixer fitted with a 3-pronged steel shaft containing small cylindrical rods on the end of each prong. The pronged shaft was fitted inside a 3-liter polyethylene jug to which the FW was added.

The FW was fluffed in this apparatus for 2-3 min. The consistency of the fluffed FW was then determined and the appropriate amount of wood placed in the reaction flask.

REACTION CONDITIONS AND PROCEDURE FOR OZONE TREATMENT OF FIBERIZED WOOD

The reaction conditions used for ozonation of FW are given in Table XXX.

TABLE XXX

REACTION CONDITIONS FOR OZONATION OF FIBERIZED WOOD

Consistency (%) - 45.0-46.1	Ozone line flow rate (liter/min) - 3.0
O.d. FW charge (g) - 60.0	Sample line flow rate (liter/min) - 1.0
Temperature (°C) - 10	Corona discharge power (v) - 120
FW pH - 6.0	Ozonator pressure (psig) - 8.0

Prior to ozonation the ozone generator and reaction apparatus were purged with oxygen for 45 min. The ozonator was started and allowed to run for 2 min before the ozone-oxygen gas flow was diverted (via 3-way stopcock systems) from the large ozone trap to the reaction apparatus. The gas flow was diverted back to the large ozone trap (see Fig. 57) at the end of the reaction.

HYDROGEN PEROXIDE CARRY-OVER EXPERIMENT

In this experiment, oxygen was passed over FW treated with 5% hydrogen peroxide (based on o.d. FW). The exit gases from the reaction flask containing the FW flowed into an ozone trap (5% KI solution). The amount of H_2O_2 carried over into the trap was determined by titration.

A blank test, where oxygen was bubbled directly into an ozone trap, was also performed. The amount of oxygen that reacted with the KI solution was

determined (by titration) and expressed as hydrogen peroxide for comparative purposes.

PROCEDURE

The ozone generator was first purged with oxygen for 15 min. A 500 mL gas-washing bottle, fitted with a gas dispersion tube, and filled with 5% KI solution was connected to the main ozone line. The ozone line and sample line flow rates were adjusted to 3 and 1 liter/min, respectively. Oxygen was run through the washing bottle for 30 min to serve as a blank test for residual ozone left in the generator and to see if oxygen reacted, to any extent, with the KI solution.

A sample consisting of 36 g o.d. FW was prepared as for ozone treatment and allowed to air-dry for 90 min until it reached the desired consistency of approximately 65%. The FW was then treated with a hydrogen peroxide solution consisting of 6.0 mL 30% H_2O_2 and 18.5 mL deionized water. This corresponded to a hydrogen peroxide concentration of 5%, based on o.d. FW, and a consistency of approximately 45%.

The hydrogen peroxide solution was sprayed on the FW immediately before it was placed in a 3-liter reaction flask and attached to the reactor. The reaction flask was cooled in an ice bath during the experiment.

Oxygen was passed over the FW for 30 min at a flow rate of 3.0 liters/min and an ozonator pressure of 7.9 psig. A 500 mL gas-washing bottle, filled with 5% KI solution, was attached to the exit gas line of the reactor to trap any H_2O_2 that was carried over in the oxygen stream from the FW.

At the end of the test period, the KI solution was acidified with 4N H_2SO_4 and titrated with 0.1N $Na_2S_2O_3$ to determine if hydrogen peroxide had passed into the solution. A similar titration was performed with the KI solution from the blank run.

In both experiments, only 0.0017 g of hydrogen peroxide was detected in the ozone traps (KI solutions). Thus it was concluded oxygen did not react, to any significant extent, with the KI solutions in the ozone traps. It was also concluded that any hydrogen peroxide formed during ozonation of FW would not be carried over in the gas stream and adversely affect the accuracy of the ozone consumption measurements.

PROCEDURE FOR ACID-WASH OF UNTREATED WOOD

A sample consisting of 19.08 g o.d. FW, which had been prepared as for ozone treatment, was washed in 1000 mL of hot (90°C), deionized water whose pH had been adjusted to 2.5 with acetic and oxalic acids. The FW was thoroughly mixed with the acidic water and allowed to soak (with frequent stirring) for approximately 15 min.

The fiberized wood was then dewatered and rewashed with 2 more portions of hot, deionized water. A final dewatering was followed by consistency and washed yield determinations. The washed yield was 98.6%. This yield was compared with the yield of 90.8% found for 5% ozone-treated FW. The filtrate pH of the 5% ozonized FW was also 2.5.

Based on a comparison of these results, it was concluded more than an acidic wash was required to effect solubilization of FW components to the extent observed for ozone treatment. Thus ozonation must be chemically modifying the FW

constituents in some manner to effect their solubilization, in addition to degrading a portion of the FW to water-soluble acids. Acetic and oxalic acids were chosen for use in this experiment since they are expected reaction products from ozonation of FW (2).

ANALYTICAL PROCEDURES

SURFACE AREA

The total surface area of the untreated FW was determined by gas adsorption using a Perkin-Elmer-Snell sorptometer. An argon-nitrogen gas mixture was used in the determinations and measurements were based on the BET point B method (82).

The FW was prepared as for ozone treatment and then air-dried in a constant temperature humidity room for 3 days. A glass sample tube was filled with 0.5-0.6 g of FW, connected to the sorptometer, and purged with the gas mixture for 15 min. The sample tube was immersed in a water bath at room temperature during the purging.

After purging, the sample tube was removed from the water bath and slowly lowered into a dewar flask filled with liquid nitrogen. The instrument recorder was turned on, and a gas adsorption curve was obtained. The sample tube was then removed from the liquid nitrogen and returned to the water bath. A gas desorption curve was now obtained.

The surface area measurement was performed in triplicate. Measurements were also made on a Whatman filter paper, which served as a reference for calculating the surface area of the FW. The adsorption and desorption curve areas were estimated on an integrator.

An example of the surface area calculation and the results obtained for untreated FW and Whatman filter paper are given in Table XXXI.

TABLE XXXI

GAS ADSORPTION CURVE AREAS

Sample	Adsorption	Desorption	Average
FW-1	2786	2944	2865
FW-2	3007	2834	2921
FW-3	2577	2805	2691
Whatman	10336	10075	10206

ASSUMPTION: Whatman filter paper has a surface area of 1.000m^2/g o.d. paper.

Calculation of Fiberized Wood Surface Area

The reference sample weight was 0.7696 g, therefore its surface area is 0.7697 m^2/g.

The oven-dry sample weights for FW were: FW-1 = 0.5234 g; FW-2 = 0.5311 g; and FW-3 = 0.4811 g. For FW-1:

$$\frac{0.7697\ m^2/g}{10{,}206\ \text{area units}} = \frac{X}{2865\ \text{area units}}$$

$$X = 0.216\ m^2/g$$

Since the weights of the FW samples were less than that of the reference sample, the calculated surface areas were adjusted accordingly.

$$\frac{0.7697\ g}{0.5235\ g} \times 0.216\ m^2/g = 0.318\ m^2/g$$

Thus the surface area of FW Sample 1 is 0.318 m^2/g.

The surface areas determined for the three untreated fiberized wood samples are given in Table XXXII.

TABLE XXXII

UNTREATED FIBERIZED WOOD SURFACE AREA

Sample	Surface area, m^2/g
FW-1	0.318
FW-2	0.319
FW-3	0.325
	Av. = 0.321

Ozone Consumption

The amount of ozone consumed by the FW was determined by titrating acidified aliquots of 5% KI solution, which had been allowed to react with ozone, with 0.1N $Na_2S_2O_3$. The aliquots were removed from the gas-washing bottles attached to the ozonator sample line and the reactor exit line. The amount of ozone consumed by the FW was calculated as shown below:

(g ozone from sample line)(split factor) - (g ozone off FW) =

(g ozone consumed) by FW

Active Oxygen

The active oxygen content of the ozone-treated FW was determined according to a modification of the method developed by Hearne (83). Immediately after completion of a reaction, a 4.00 g a.d. sample of ozonized FW was placed in a 500 mL Erlenmeyer flask to which 250 mL of deionized water had been added. The slurry was stirred for 5 min on a magnetic stirrer and then filtered through a 350 mL coarse, fritted-glass crucible.

The effluent was collected and returned to the flask. Approximately 50 mg of sodium carbonate was added to the solution followed by 10 mL of 4N H_2SO_4. Another 50 mg addition of sodium carbonate was followed by 5 g of KI and 5 drops

of a 3% ammonium molybdate solution. The mixture was stirred and then titrated with 0.1N $Na_2S_2O_3$, using thyodene as the indicator.

The active oxygen content of the ozonized FW, expressed as percent H_2O_2, was calculated as shown below:

$$(\text{Normality } Na_2S_2O_3)(\text{mL } Na_2S_2O_3)(0.017) = \text{g } H_2O_2$$

$$\text{g } H_2O_2/\text{g o.d. FW} = \% \text{ active oxygen (as } H_2O_2 \text{ based on o.d. FW)}$$

Klason Lignin

The Klason lignin content of FW were determined using TAPPI Standard Method T 222.

Acid-Soluble Lignin

The acid-soluble lignin content of FW were determined according to the method of Pearl and Busche (84). The absorbance of the filtrates from the Klason lignin determinations was measured at 208 nm. The acid-soluble lignin content was then calculated using the following formula:

$$A = abc$$

where A = absorbance of filtrate

a = absorptivity of acid-soluble lignin at 208 nm = 105 liters/g cm (based on lignin calibration curve)

b = cell size = 1 cm

c = concentration of acid-soluble lignin in filtrate (g/liter)

Methoxyl

The methoxyl content of FW was determined according to a slight modification of IPC Method 18. Fresh reagents were used for each determination, including blanks, and 3.3 mL propionic anhydride was substituted for 3 g of phenol.

Carboxyl

The carboxyl content of untreated and ozonated FW was determined as described in TAPPI Standard Method T 237. Sample size was reduced from 2 g o.d. FW to 1 g.

The carboxyl content of the water washings from ozonated FW was determined by potentiometric titration. An ozonized FW sample of approximately 5.00 g (oven-dry) was throughly washed with 250 mL and 200 mL portions of hot (90°C), deionized water. After each washing, the FW slurry was filtered through a 350 mL coarse, fritted-glass filtering funnel. The washings were collected, combined, and titrated with CO_2-free 0.1N NaOH, with agitation after each incremental addition of base.

The pH change during the titration was monitored on a Beckman Zeromatic pH meter. A pH value of 7.0 was chosen as the end point of the titration. This coincided well with the inflection point observed when a plot of pH versus milliliters of base was made (Fig. 58).

Holocellulose Isolation

Holocellulose samples, used for viscosity determinations, were isolated from untreated and ozonated FW using the procedure of Wegener (85). The reaction conditions used for holocellulose isolation are given in Table XXXIII.

The active chlorine was provided by 4 equal additions of sodium chlorite. The pH was controlled with acetic acid. Following reaction, the holocellulose was throughly washed in hot, deionized water and air-dried.

Viscosity

Cuene viscosities were determined on holocellulose samples isolated from untreated and ozonated FW, according to IPC Method 32.

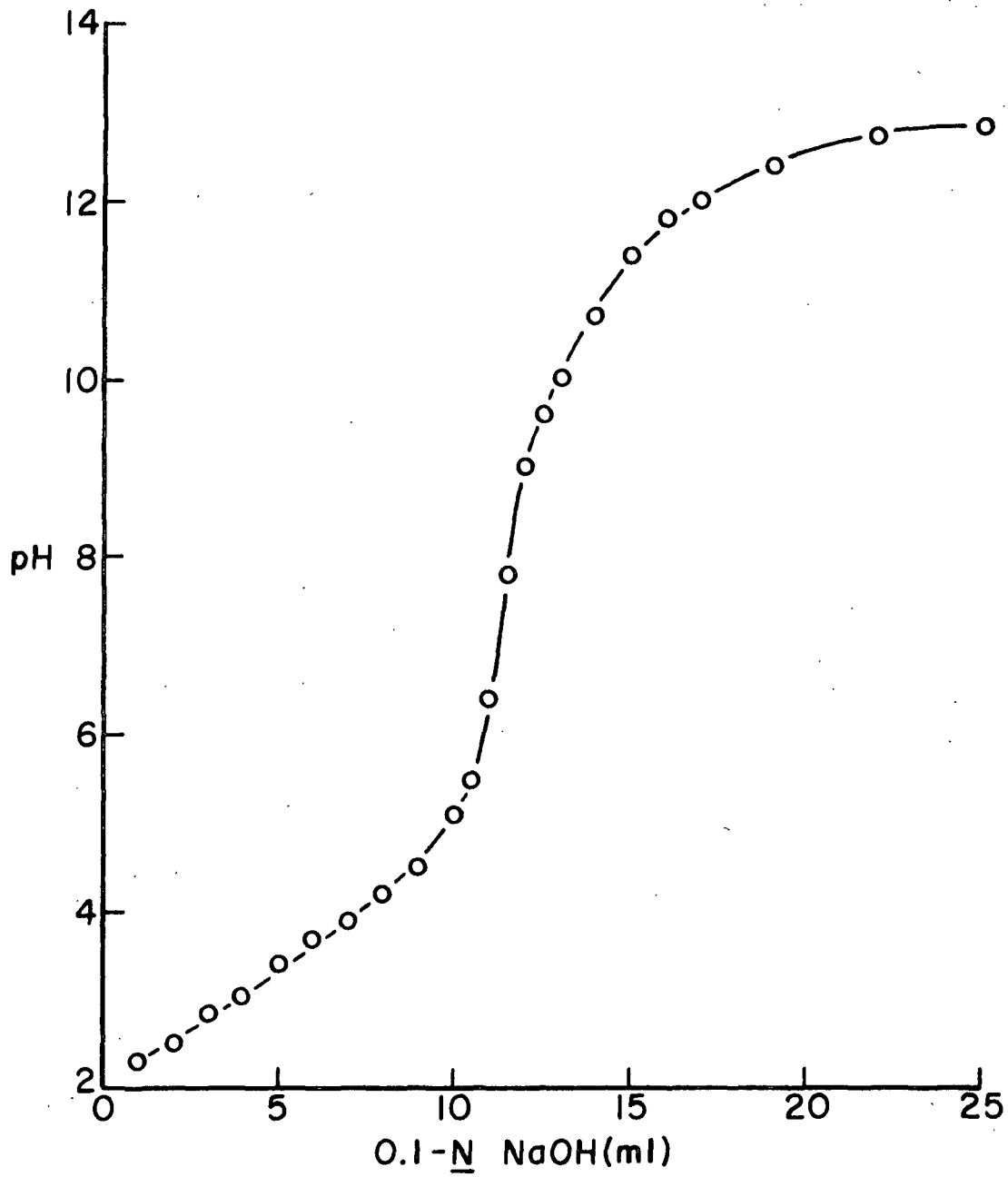

Figure 58. pH versus Milliliters NaOH for Wash Filtrate from 5% Ozonized FW

TABLE XXXIII

REACTION CONDITIONS FOR HOLOCELLULOSE ISOLATION

FW charge (o.d. g) - 10.00	Consistency (%) - 3.0
Time (hr) - 24.0	Active chlorine (%) - 237
Temperature (°C) - 50.0	pH - 4.0

Carbohydrate

The sugar analysis of untreated and ozonated FW, as well as isolated reaction products, was determined using the gas chromatographic method of Borchardt and Piper (86). In this method, the monosaccharides present in the hydrolyzed sample were reduced to their corresponding alditols with sodium borohydride. Acetylation with acetic anhydride and sulfuric acid was followed by precipitation of this mixture into ice water. The acetylated alditols were then extracted with methylene chloride for injection onto the chromatograph.

The gas chromatograms obtained for the isolated, water-soluble reaction products are shown in Fig. 59 and 60. The individual peaks were identified according to retention times as indicated in Table XXXIV.

The unidentified peaks at the two lowest retention times probably represented sugar fragments containing less than 5 carbon atoms (87). Various glycols, glycerols, and tetratol derivatives formed from ozone oxidation of the larger sugar molecules are possibilities.

The chromatograms (Fig. 59 and 60) indicated there were more degraded sugar fragments at the higher ozonation level (7%). This increase was paralleled by a decrease in the amount of xylan, mannan, galactan, and glucan found at 7% ozone, as compared to 5% ozone. This suggested ozonation resulted in further degradation of these sugars to smaller fragments.

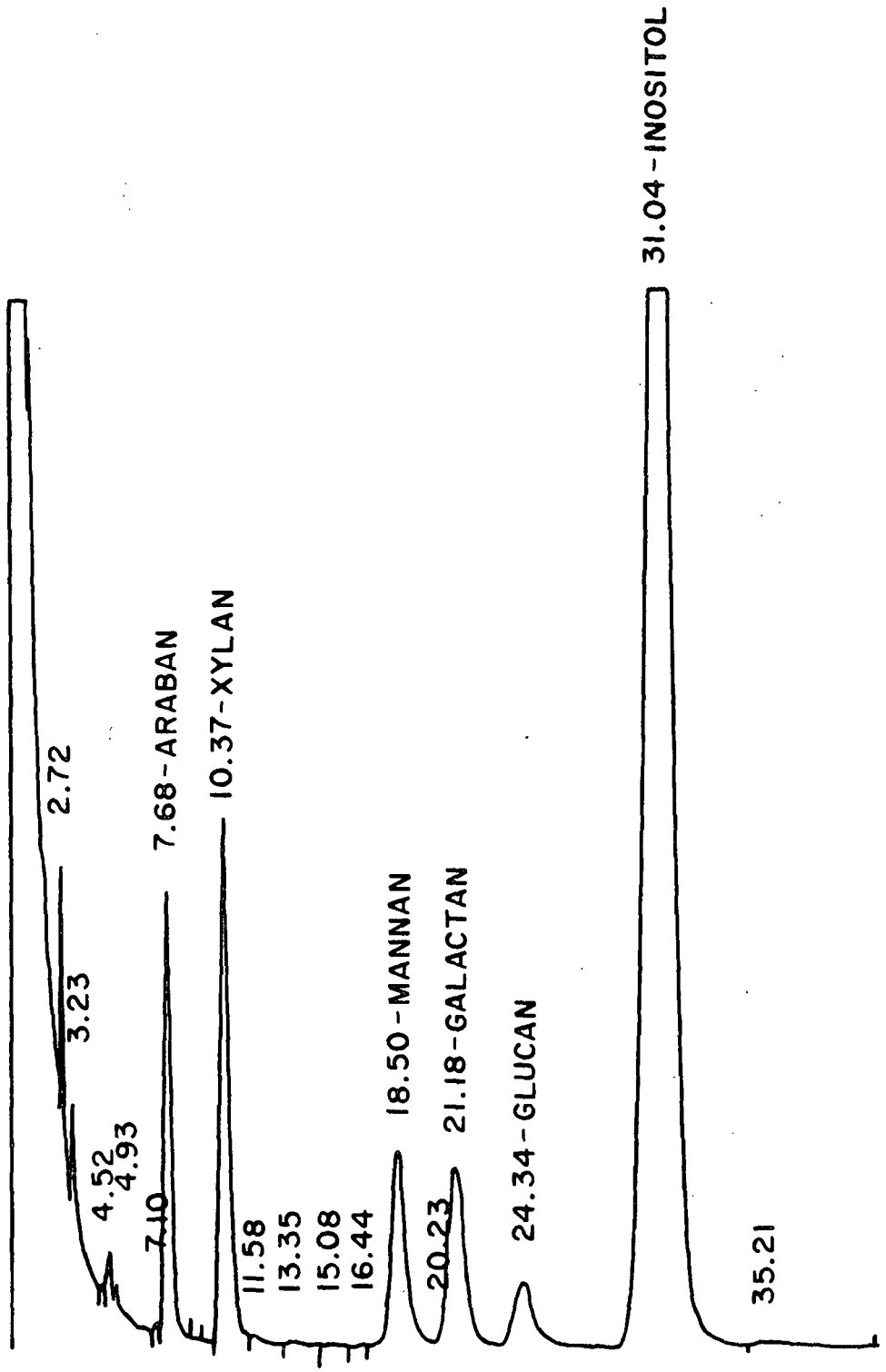

Figure 59. Gas Chromatogram of Water-Soluble Sugars Isolated from 5% Ozone-Treated Fiberized Wood

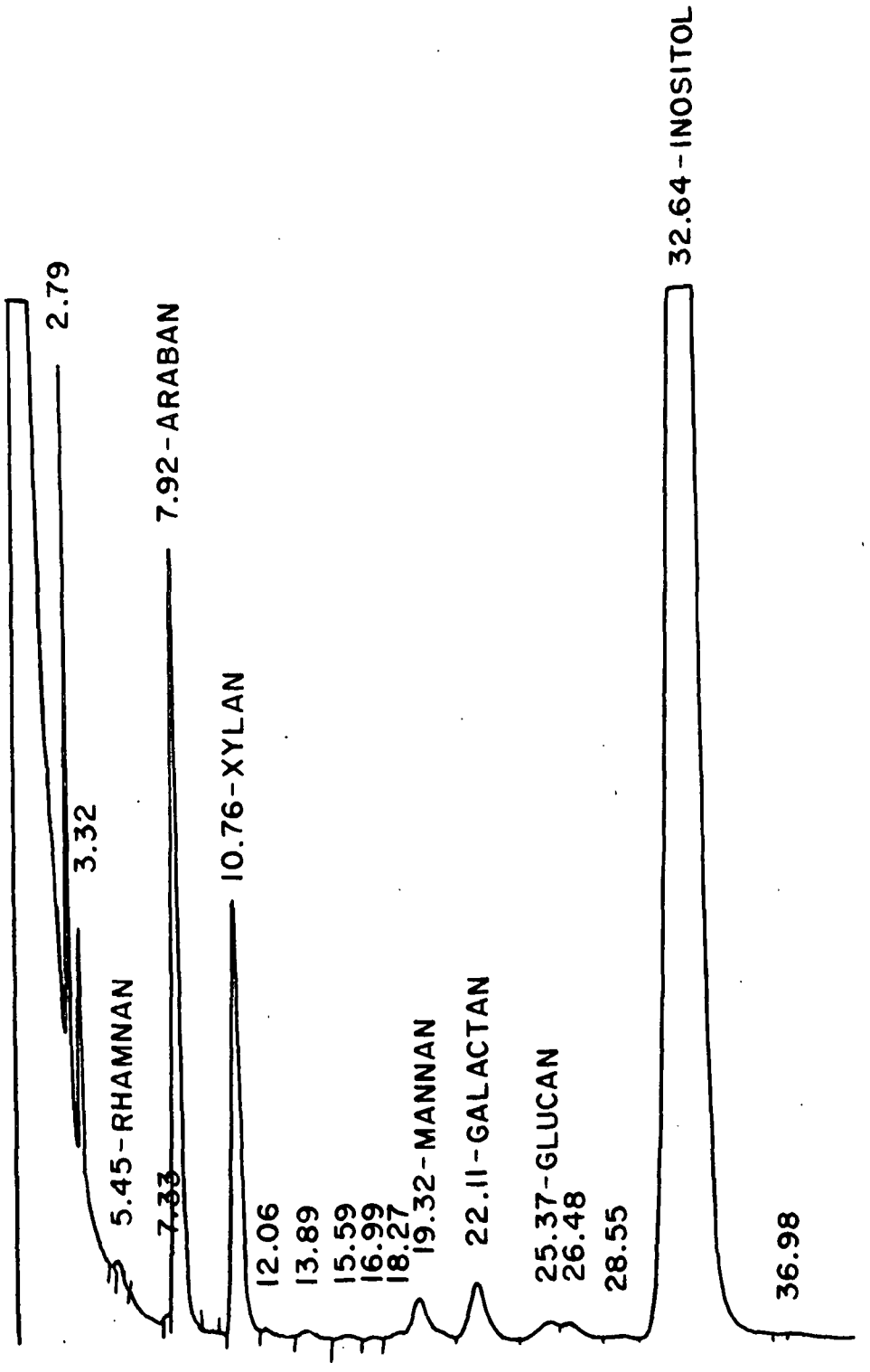

Figure 60. Gas Chromatogram of Water-Soluble Sugars Isolated from 7% Ozone-Treated Fiberized Wood

TABLE XXXIV

RETENTION TIME OF WATER-SOLUBLE SUGARS

Sugar	Retention Time, min	
	5% Ozone	7% Ozone
?	2.72	2.79
?	3.23	3.32
Rhamnan	-	5.45
Araban	7.68	7.92
Xylan	10.37	10.76
Mannan	18.50	19.32
Galactan	21.18	22.11
Glucan	24.34	25.37

Brightness

The brightness of FW was determined according to TAPPI Standard Method T 217. It was necessary to use 6 g pads, rather than 3 g, due to the poor bonding nature of FW.

Luminance Reflectance

The luminance reflectance of FW was determined using TAPPI Standard brightness handsheets (6 g), at a wavelength of 557 nm. The same procedure as for brightness determinations was followed.

Oxalic Acid

The percent oxalic acid, in a sample of isolated reaction products from 5% ozonized FW, was determined using the gas chromatographic method of Dence, et al. (88). The isolated reaction products were dried over P_2O_5 and then methylated with methanolic HCl. This converted the oxalic acid to its methyl ester.

The methylated material was then subjected to gas chromatographic analysis. The concentration of methyl oxalate was determined on an external standard basis using calcium oxalate. The gas chromatogram obtained for this analysis is shown in Fig. 61.

Phenolic Hydroxyl

The phenolic hydroxyl content of untreated and ozonated FW was determined using a selective methylation technique similar to that developed by Andrews and Des Rosiers (74). Fiberized wood samples were methylated at pH = 11.1 with dimethyl sulfate.

The calculation of phenolic hydroxyl content of FW, based on methoxyl content of unmethylated and methylated wood, is given in Appendix XVIII.

PROCEDURE FOR METHYLATION OF FIBERIZED WOOD

Fiberized wood samples were methylated according to a procedure similar to that used by Andrews and Des Rosiers (74), and later by Johnson, et al. (5). The apparatus constructed for methylation of FW is shown in Fig. 62. The reaction conditions used for methylation of FW are given in Table XXXV.

The FW was Wiley milled to pass through a No. 80 mesh screen. A sample of the Wiley milled FW was weighed, dried at 105°C, and reweighed to determine its consistency. A sample of air-dry milled FW corresponding to 1.0000 g of o.d. FW was weighed out and placed in the reaction flask. Next, 100 mL of distilled water and a magnetic stirring bar were added. The flask was stoppered and placed in the heating mantle where it was vigorously stirred and gradually heated up to temperature (40°C) over a period of several hours.

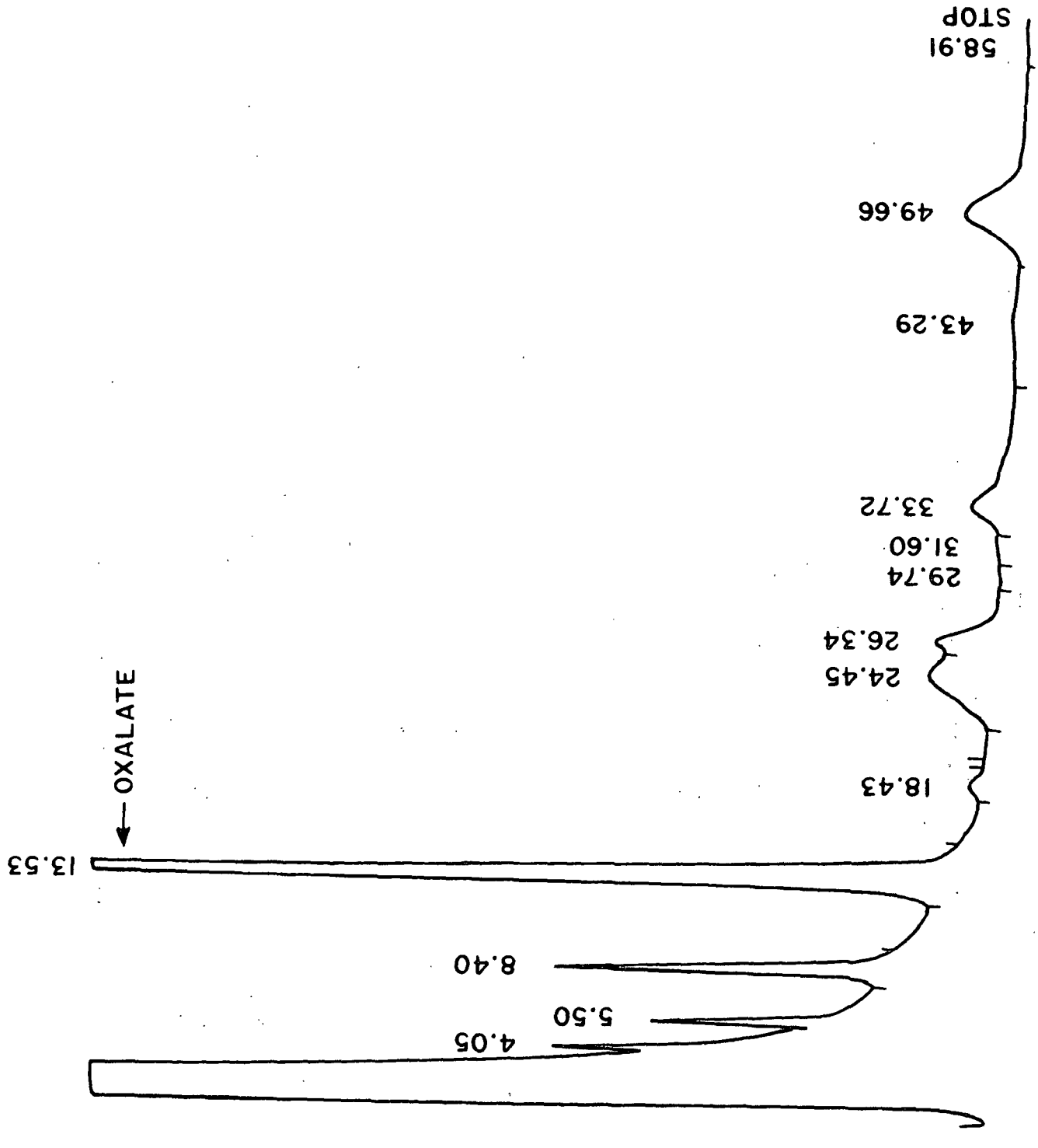

Figure 61. Gas Chromatogram for Oxalic Acid Analysis

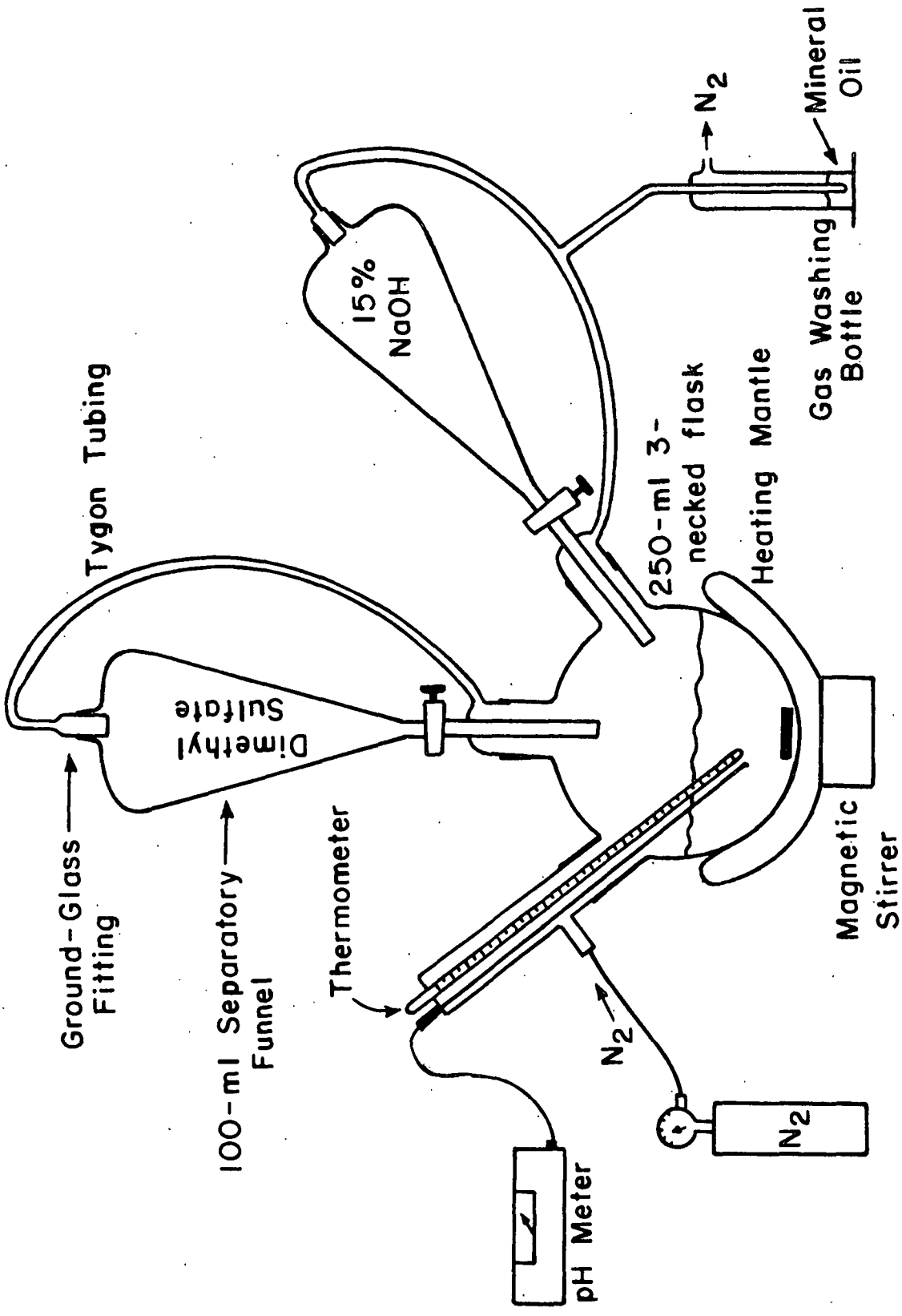

Figure 62. Apparatus for Methylation of Fiberized Wood

TABLE XXXV

REACTION CONDITIONS FOR METHYLATION OF FIBERIZED WOOD

FW charge (o.d. g) - 1.000	Dimethyl Sulfate charge (mL) - 1.5
Consistency (%) - 1.0	Sodium Hydroxide concentration (%) - 15.0
Temperature (°C) - 40 ± 2	

The two separatory funnels (see Fig. 62) were filled with dimethyl sulfate and 15% sodium hydroxide, respectively, and inserted into the reaction flask. The combination pH electrode and thermometer were also fitted into the flask and a nitrogen purge was begun. The apparatus was purged with nitrogen for 15 min and then the pH of the woodmeal slurry was adjusted to the desired value by addition of sodium hydroxide.

At the start of the reaction, approximately 12 drops of dimethyl sulfate was added to the reaction flask. Additions of this same amount of dimethyl sulfate were repeated every 10 min. Sodium hydroxide was added dropwise whenever necessary to control pH at the desired level. The pH was monitored on a Beckman Zeromatic pH meter.

Typically, the dimethyl sulfate charge (1.5 mL) was exhausted within 70-80 min of reaction. Addition of sodium hydroxide was continued until the pH stabilized. This usually required another 20-40 min, thus the entire methylation was completed in approximately 2 hr.

After completion of the reaction, the separatory funnels, thermometer, and pH electrode were removed from the reaction flask. The flask was then stoppered and allowed to stand overnight.

The methylated FW samples were filtered on a 60 mL glass crucible, washed throughly with hot, distilled water, and allowed to air-dry. Upon completion of air-drying, consistency, methylated yield, and methoxyl content were determined.

PROCEDURE FOR RECOVERY OF WATER-SOLUBLE REACTION PRODUCTS

The water-soluble reaction products removed during washing of ozonated FW were concentrated under vacuum, at a temperature of 50°C, to a volume of about 200 mL. The 200-mL samples were then frozen in an acetone-dry ice bath and freeze-dried to recover the reaction products. The products were stored away from light in a desiccator.

PREPARATION OF FIBERIZED WOOD FOR INFRARED ANALYSIS

PELLET FORMATION

Infrared spectra were obtained from transmittance measurements made on potassium chloride pellets containing finely pulverized FW. To prepare the pellets, Wiley milled FW (No. 60 mesh) was placed in stainless steel capsules and ground for six periods of 5 min on a mixer mill. Care was taken to cool the material between grinding periods to prevent overheating. Reagent grade potassium chloride was powdered in the same manner.

The finely powdered FW was dried in a vacuum oven at 40°C for 48 hr. A sample consisting of 2 mg of powdered FW was mixed with 200 mg of powdered KCl and formed into a pellet using a conventional pellet press and die. Vacuum was applied for 5 min, followed by a force of 19,000 lb for 10 min. Upon removal from the press, the pellets were stored over Drierite to prevent moisture contamination.

NEUTRALIZATION OF FIBERIZED WOOD SAMPLES

An air-dried sample of Wiley milled FW ($\sim$1 g) was dispersed in 40 mL of distilled water. The sample was placed on a magnetic stirrer and a combination pH electrode inserted into the solution. The solution was rapidly stirred as incremental additions of 0.01N NaOH were made. The pH of the solution was monitored on a Beckman Zeromatic pH meter. After the solution stabilized at a pH = 9.2, the FW slurry was dewatered and throughly washed with distilled water.

The washed, neutralized sample was divided in half. One-half of the FW sample was air-dried and made into a KCl pellet as described previously. The remainder of the sample was used in the acidification procedure.

ACIDIFICATION OF FIBERIZED WOOD SAMPLES

Approximately 0.5 g of the washed, neutralized FW sample was redispersed in 40 mL of distilled water. The sample was placed on a magnetic stirrer and a combination pH electrode inserted into the solution. The solution was rapidly stirred as incremental additions of 0.1N HCl were made. The pH of the solution was monitored on a Beckman Zeromatic pH meter. After the solution stabilized at a pH = 2.1, the FW slurry was dewatered and throughly washed with distilled water until the effluent gave no reaction with 5% silver nitrate. The acidified FW was air-dried prior to pulverization and pellet preparation.

PROCEDURE FOR OBTAINING INFRARED SPECTRA

Infrared transmission spectra of holocellulose samples and isolated reaction products were obtained on a Perkin-Elmer Model 700 dispersive infrared spectrometer.

All transmission spectra obtained for FW samples were made on a Nicolet 7199 Fourier transform infrared spectrometer.

The FT-IR measurements were obtained by taking 200 scans (interferograms) per sample pellet, with resolution set at 2 wavenumbers. The spectra were plotted as percent transmittance versus wavenumbers (cm^{-1}) on a scale of 400-4000 wavenumbers. After plotting, each spectrum was stored in the magnetic disc memory system of the computer.

DIFFERENCE SPECTRA

The FT-IR difference or "subtraction" spectra were obtained as described in the following paragraphs.

The two transmission spectra of interest were displayed on the scope and balanced in the C-H stretch region ($\sim$ 2900 cm^{-1}) until they appeared equal in intensity. This balancing process involved multiplication of the reference spectrum (usually untreated FW) by an appropriate weighting factor that equalized the intensity of the reference and sample spectrum.

Next, the two spectra were converted from transmittance to absorbance by the computer. The reference spectrum was multiplied by the appropriate weighting factor and then subtracted from the sample spectrum to give the difference spectrum. An example is given below:

$$\underset{\text{Ozonated FW}}{(\text{Sample spectrum})} - \underset{\text{Untreated FW}}{(\text{Reference spectrum})}(\text{Wt. factor}) = \text{Difference spectrum}$$

The difference spectra obtained in this manner were plotted as absorbance versus wavenumbers (cm^{-1}). Base line correction (leveling of the spectra) was performed if necessary.

PROCEDURE FOR MEASURING ABSORBANCE OF FT-IR SPECTRA

TRANSMISSION SPECTRA

In several cases (i.e., calculation of normalized spectra) it was desirable to obtain absorbance measurements, at particular wavelengths, from FT-IR transmission spectra. This required converting transmittance values to absorbance. This was done through the use of Equation (1).

$$A = \log_{10}(1/T) \quad (1)$$

where A = absorbance

T = transmittance

The value of T was determined from the transmission spectrum as shown in Fig. 63. Base lines used for measurement of individual peaks were drawn through points in the spectrum where there was no apparent absorption.

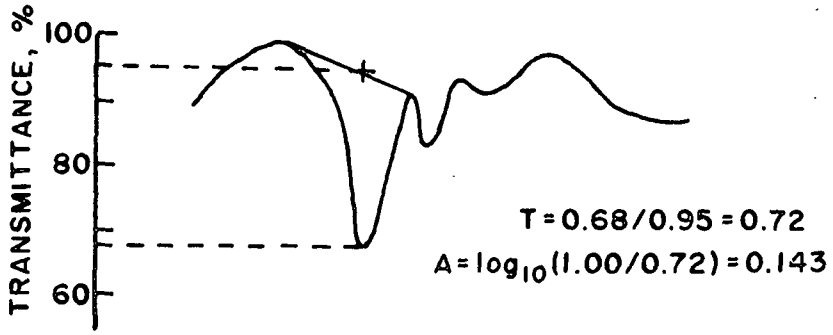

Figure 63. Procedure for Converting from Percent Transmittance to Absorbance

DIFFERENCE SPECTRA

Absorbance values for FT-IR difference spectra were obtained directly. Base lines were drawn through points in the spectra where no absorbance was observed. The height of the peak of interest was measured from the base line and multiplied by the appropriate absorbance units (usually 0.05 absorbance units/25.4 mm).

PROCEDURE FOR CALCULATING NORMALIZED SPECTRA

Normalized spectra were obtained by combining the absorbance value determined from an untreated FW transmission spectrum with the corresponding absorbance values obtained from the ozonated FW minus untreated FW difference spectra. An example is shown below:

Untreated FW spectrum (absorbance value)	+	Ozonated FW minus untreated FW difference spectra (absorbance values)	=	Normalized spectra (absorbance values)

SUGGESTIONS FOR FURTHER RESEARCH

It would be of interest to perform a similar study using an alkali-fiberized hardwood as the substrate. It could then be determined if hardwood lignin is more susceptible to ozone modification than softwood lignin. Since hardwoods are easier to pulp than softwoods, it would also be interesting to compare the extent of ozone delignification observed for the different substrates.

This study showed significant delignification of fiberized wood can be achieved using ozone, with the extent of delignification being a direct function of ozone consumption. It would be of interest to determine if ozone's effectiveness as a delignification agent decreases at ozone consumption levels significantly higher than those used in this study. The possibilities of a multistage ozone delignification process could also be explored. The fiberized wood could be subjected to several ozone treatments, with wood washing performed between each stage to remove degraded lignin. The degraded lignin may consume ozone which could otherwise serve to further delignify the wood.

A study involving identification of the water-soluble reaction products formed from the ozone degradation of fiberized wood could be helpful in formulating particular ozone-lignin reaction mechanisms characteristic of a wood system. A molecular weight determination on the solubilized products would give evidence as to whether the lignin is solubilized as large or relatively small fragments.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to the members of his thesis advisory committee: Dr. R. D. McKelvey, who served as the initial chairman; Dr. N. S. Thompson, who served as Chairman for the final part of the work; and Drs. R. H. Atalla and E. W. Malcolm. Their assistance and guidance is deeply appreciated.

The author would also like to express his gratitude to several staff members for their assistance in this study: Messrs. M. C. Filz, Jr., P. F. Van Rossum, and L. Borchardt.

I would like to gratefully acknowledge The Institute of Paper Chemistry for the opportunity to participate in its graduate education program and for the generous financial support so provided.

Donation of loblolly pine by Union Camp Corporation and the wood fiberization performed by the Bauer Brothers Corporation is appreciated.

I would also like to thank the Nicolet Instrument Corporation for use of their FT-IR spectrometer and especially Dr. Robert Julian for his expertise and cooperation in obtaining the spectra.

Finally, I wish to express my deepest and sincerest appreciation to my wife, Joanna, for her never-ending patience and support throughout this work.

LIST OF ABBREVIATIONS

C-9 = guaiacyl propane lignin unit

DP = degree of polymerization

FW = fiberized wood

FT-IR = Fourier transform infrared

IR = infrared

N = normal

o.d. = oven-dry

UV = ultraviolet

LITERATURE CITED

1. Soteland, N., Norsk Skogind. 28(6):165(1974).

2. Soteland, N., Norsk Skogind. 25(3):61(1971).

3. Soteland, N., Pulp Paper Mag. Can. 78(7):T157-60(1977).

4. Soteland, N., Pulp Paper Mag. Can. 75(4):T153(1974).

5. Johnson, D. C. and McKelvey, R. D., Unpublished results, The Institute of Paper Chemistry, Appleton, Wis., 1976-77.

6. Singh, R. P. and Eckert, R. C. Ozone reactions in relation to the aromatic structure of lignin: A review of selected topics in ozone chemistry. Intern. Symp. on Delignification with Oxygen, Ozone, and Peroxides, Raleigh, N.C., May, 1975.

7. Encyclopedia Chem. Tech. 14:410(1967).

8. Criegee, R., Angew. Chem. Intern. Ed. 14:11(1975).

9. Hatakeyama, H., Tonooka, T., Nakano, J., and Migita, N., J. Chem. Soc. Japan Ind. Chem. Sect. 70:2348(1967).

10. Kratzl, K., Claus, P., and Reichel, G., Tappi 59(11):86-7(1976).

11. Balousek, P. J. The effects of ozone upon lignin-related model compounds containing a β-aryl ether linkage. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1979.

12. Kojima, Y., Miura, K., and Kayama, T., Res. Bull. Expt. Forests, Hokkaido Univ. 35(1):165-84(1978).

13. Katuscak, S., Hrivik, A., and Mahdalik, M., Paperi Puu 53(9):519-24(1971).

14. Hatakeyama, H., Tonooka, T., Nakano, J., and Migita, N., Dogyo Kaguku Zasshi 71(8):1214-17(1968).

15. Katuscak, S., Rybarik, I., Paulinyova, E., and Mahdalik, M., Paperi Puu 53(11):665-70(1971).

16. Katuscak, S., Hrivik, A., and Macak, K., Paperi Puu 54(4a):201-6(1972).

17. Katuscak, S., Hrivik, A., Katuscakova, G., and Schiessl, O., Paperi Puu 54(12):861-70(1972).

18. Soteland, N., Norsk Skogind. 25(5):135(1971).

19. Hergert, H. L., J. Org. Chem. 25:405(1960).

20. Adler, E. and Marton, J., Acta Chem. Scand. 15:357(1961).

21. Bailey, P. S. and Wife, H. M., J. Org. Chem. 30:3037(1965).

22. Erickson, R. E., Hansen, R. T., and Harkins, J., J. Am. Chem. Soc. 90:6777 (1968).

23. Hoigne, J. and Bader, H., Science 190:782-6(1975).

24. Katai, A. A. and Schuerch, C., J. Polymer Sci., Part A-1, 4:2683-2703(1966).

25. Singh, R. P. and Secrist, R. B., Tappi 54(4):581-4(1971).

26. Schuerch, C., J. Polymer Sci., Part C, 2:79-95(1963).

27. Rothenburg, S., Robinson, D., and Johnsonbaugh, D., Tappi 58(8):182-5(1975).

28. Szopinski, R., Przeglad Papier. 31(10):391-6(1975).

29. Lindholm, C., Paperi Puu 59(4a):217-32(1973).

30. Oswa, Z., Erby, W. A., Sarkanen, K. V., Carpenter, E., and Schuerch, C., Tappi 46(2):84-8(1963).

31. Moore, W. E., Effland, M., Sinha, B., Burdick, M. P., and Schuerch, C., Tappi 49(5):206-9(1966).

32. Kratzl, K., Claus, P., Lonsky, W., and Gratzl, J. S., Wood Sci. Tech. 8 (1):35(1974).

33. Kratzl, K., Gratzl, J. S., and Claus, P., Adv. Chem. Series 59:157(1966).

34. Aoyagi, T., Hosoya, S., and Nakano, J., Japan Wood Res. Soc. 21(9):532-4 (1975).

35. Kolboe, S. and Ellefson, O., Tappi 45(2):163-9(1962).

36. Vander Linden, N. G. Studies on chlorine dioxide modification of lignin in wood. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1974.

37. Bolker, H. I. and Somerville, N. G., Pulp Paper Mag. Can. 64:T187-93(1963).

38. Marton, J. and Sparks, H. E., Tappi 50(7):363-8(1967).

39. Hergert, H. L. In Sarkanen and Ludwig's Lignins: Occurrence, formation, structure, and reactions. p. 267-97. New York, Wiley-Interscience, 1971.

40. Mitchel, A. J., Aust. J. Chem. 19:2285(1966).

41. Ekman, K. H. and Lindberg, J. T., Paperi Puu 42:21(1960).

42. Azhar, M. R. and Wayman, M., Pulp Paper Mag. Can. 71:T81-6(1970).

43. Marton, J., Adler, E., and Persson, K. I., Acta Chem. Scand. 15(2):384-92 (1961).

44. Whitsitt, W. J., Krueger, W. C., and John, B., Unpublished results, The Institute of Paper Chemistry, Appleton, Wis., 1978.

45. Lindholm, C. A. and Gummerus, M., Paperi Puu 60(11):653-62(1978).

46. Lewis, H. F., Tappi 33(6):299-301(1950).

47. Leopold, B., Tappi 44(3):230-2(1961).

48. Browning, B. L. and Bublitz, L. O., Tappi 36(10):452-8(1953).

49. Brauns, F. E. and Brauns, D. E. The Chemistry of Lignin. p. 141. New York, Academic Press, 1960.

50. Browning, B. L. Methods of Wood Chemistry. Vol. II. p. 717-18. New York, Interscience, 1967.

51. Adler, E., Wood Sci. Tech. 11:169-218(1977).

52. Rydholm, S. A. Pulping Processes. p. 190. New York, Interscience, 1967.

53. Crozier, T. E. Oxygen-alkali degradation of loblolly pine dioxane lignin: Changes in chemical structure as a function of time of oxidation. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1978.

54. Rydholm, S. A. Pulping Processes. p. 164. New York, Interscience, 1967.

55. Borchardt, L., personal communication, The Institute of Paper Chemistry, Appleton, Wis., 1979.

56. Wise, L. E. and Ratliff, E. K., Anal. Chem. 19:459(1947).

57. Ellefsen, O. and Tonnesen, B. A. In Bikales and Segal's Cellulose and Cellulose Derivatives. Part IV. p. 284. New York, Wiley-Interscience, 1971.

58. Bailey, P. S. and Lerdal, D. A., J. Am. Chem. Soc. 100:18(1978).

59. Bailey, P. S., Chem. Rev. 58:984(1958).

60. Rydholm, S. A. Pulping Processes. p. 886. New York, Interscience, 1967.

61. Hagglund, E. and Sandelin, O., Svensk Kem. Tidskr. 46:83(1934).

62. Browning, B. L. Methods of Wood Chemistry. Vol. II. p. 660. New York, Interscience, 1967.

63. Bjorkman, A., Svensk Papperstid. 59:477(1956).

64. Bjorkman, A., Svensk Papperstid. 60:285(1957).

65. Wise, L. E. and Jahn, E. C. Wood Chemistry. p. 452. New York, Reinhold, 1967.

66. Bellamy, L. J. The Infrared Spectra of Complex Molecules. p. 184. New York, Wiley and Sons, 1975.

67. Dyer, J. R. Infrared Spectroscopy. p. 33-9. Prentice-Hall, 1965.

68. Flett, M. St. C., J. Chem. Soc. 1951:962-7.

69. Cross, L. H. and Rolfe, A. C., Trans. Faraday Soc. 47:354(1951).

70. Brooks, C. J. W., Eglinton, G., and Morman, J. F., J. Chem. Soc. 1961:106-16.

71. Bellamy, L. J. The Infrared Spectra of Complex Molecules. p. 150-1, 184, 204. New York, Wiley and Sons, 1975.

72. Adler, E. and Marton, J., Acta Chem. Scand. 1:75(1959).

73. Bellamy, L. J. The Infrared Spectra of Complex Molecules. p. 124. New York, Wiley and Sons, 1975.

74. Andrews, D. H. and Des Rosiers, P., Pulp Paper Mag. Can. 67:T119(1966).

75. Rydholm, S. A., Svensk Papperstid. 62:554(1959).

76. March, J. Advanced Organic Chemistry: Reactions, Mechanisms, Structure. p. 220. New York, McGraw-Hill, 1968.

77. Rydholm, S. A. Pulping Processes. p. 153. New York, Interscience, 1967.

78. Adler, E., Miksche, G. E., and Johansson, B., Holforschung 22:171(1968).

79. Pew, J. C., Tappi 40:553(1957).

80. Chang, H. M., Cowling, E. B., Brown, W., Adler, E., and Miksche, G. M., Holzforschung 29:153(1975).

81. Lawrence, W. J. The peroxyacetic acid degradation of lignin-related model compounds. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1978.

82. Mazurak, P. A. Characterization of cellulosic adsorbent surfaces by gas adsorption utilizing inverse gas chromatographic surface adsorption indices of organic adsorbate vapors. p. 155-6. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1978.

83. Hearne, D. O. The effect of the aglycon and hydroxyl orientation on alkali-oxygen degradation of methyl glycosides. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1978.

84. Pearl, I. R. and Busche, L. R., Tappi 43(12):961(1960).

85. Wegener, G., Papier 26(11):478(1974).

86. Borchardt, L. and Piper, C., Tappi 53(2):257(1970).

87. Borchardt, L., personal communication, The Institute of Paper Chemistry, Appleton, Wis., 1979.

88. Dence, C. W., Ota, M., and Durst, W. B., Tappi 56(6):139(1973).

89. Isenberg, I. H. Pulpwoods of the U.S. and Canada. p. 21. Appleton, Wis., The Institute of Paper Chemistry, 1951.

91. Chidester, G. H. and McGovern, J. N., Paper Trade J. 4:36(1938).

APPENDIX I

ADVANTAGES OF FOURIER TRANSFORM INFRARED SPECTROSCOPY

The great dependence of this study on FT-IR spectroscopy necessitates a brief discussion of its advantages as compared to conventional infrared spectroscopy.

The FT-IR system measures all wavelengths of the infrared spectrum simultaneously. Conventional (dispersive) spectrometers measure only one wavelength at a time. Thus for N different experiments, the FT-IR spectrometer is N times faster than a dispersive spectrometer or has $\sqrt{N}$ more analytical sensitivity for the same measurement time.

Unlike conventional IR spectrometers, the FT-IR instrument has no energy-limiting slits. This allows much more energy to reach the sample and subsequently the detector. More energy at the detector yields higher analytical sensitivity.

A powerful computer data system is an integral part of the FT-IR system. The data system performs the Fourier transformation and is programmed to allow the user to digitally manipulate the spectra.

The FT-IR instrument has a helium-neon laser to calibrate the wavelength of each scan; thus insuring extremely high accuracy of wavelength calibration.

The FT-IR spectrometer also has several special features that make it especially suitable for difference spectroscopy work. These include (1) a scope display that can handle up to three spectra simultaneously, thus facilitating the manipulations necessary to obtain accurate difference spectra, (2) software that provides for base line correction (effects of scattering) through

both digital filtering and straight-line fitting, (3) software consisting of several mathematical functions for smoothing noisy spectra, and (4) a large magnetic disk memory system for storing the individual spectra.

APPENDIX II

BAND ASSIGNMENTS FOR INFRARED ABSORPTION IN FIBERIZED WOOD

TABLE XXXVII

BAND ASSIGNMENTS FOR INFRARED ABSORPTION IN FIBERIZED WOOD

Wavelength, cm^{-1}	Band Origin
3400	O-H stretch
2900	C-H stretch
1725-30	C=O stretch (unconjugated)
1660	C=O stretch (conjugated)
1605	COO^- stretch
1600	C=C stretch
1510	C=C stretch
1220	C-O stretch (phenols)

[a]From references (68,72)

APPENDIX III

CHARACTERIZATION OF STARTING MATERIAL

TABLE XXXVIII

CHARACTERIZATION OF ALKALI-FIBERIZED LOBLOLLY PINE

	This Work[a]	Literature[b]
Simulated Fiberized Yields, %[c]	91.6	-
Extractives, %[d]	2.7	2.7 (89) 3.8 (90) 4.4 (47)
Klason Lignin, %	27.7	-
Acid-Soluble Lignin, %	0.4	-
Total Lignin, %	28.1	28.1 (89) 28.3 (47,90) 28.5 (48) 29.5 (56)
Methoxyl, %	4.85	4.81 (47)
Carboxyl (meq/100-g o.d. FW)	12.5	20.0 (48)
Total Surface Area (m^2/g)	0.321	-
Brightness (% at 557-nm)	23.0	-
Luminance Reflectance (% at 557-nm)	43.3	-
Carbohydrate, %		
Glucan	46.1	46.3
Mannan	11.8	10.4
Galactan	2.3	1.6 (48)
Xylan	6.5	6.9
Araban	1.2	1.1

[a] All values based on acetone-extracted, oven-dry fiberized wood except where noted.
[b] Literature values based on oven-dry loblolly pinewood.
[c] Based on oven-dry loblolly pinewood.
[d] Based on oven-dry fiberized wood.

APPENDIX IV

UNTREATED AND OZONATED FIBERIZED WOOD FT-IR TRANSMISSION SPECTRA

FT-IR transmission spectra were obtained for the following fiberized wood samples:

1. Untreated FW (Fig. 64)
2. Ozonated, unwashed FW (Fig. 65-68)
3. Ozonated, washed FW (Fig. 69-72)

Note: The hyperfine structure appearing in several of the transmission and difference spectra (e.g., Fig. 66, 76, 105) is a result of interference from water vapor, not instrument noise.

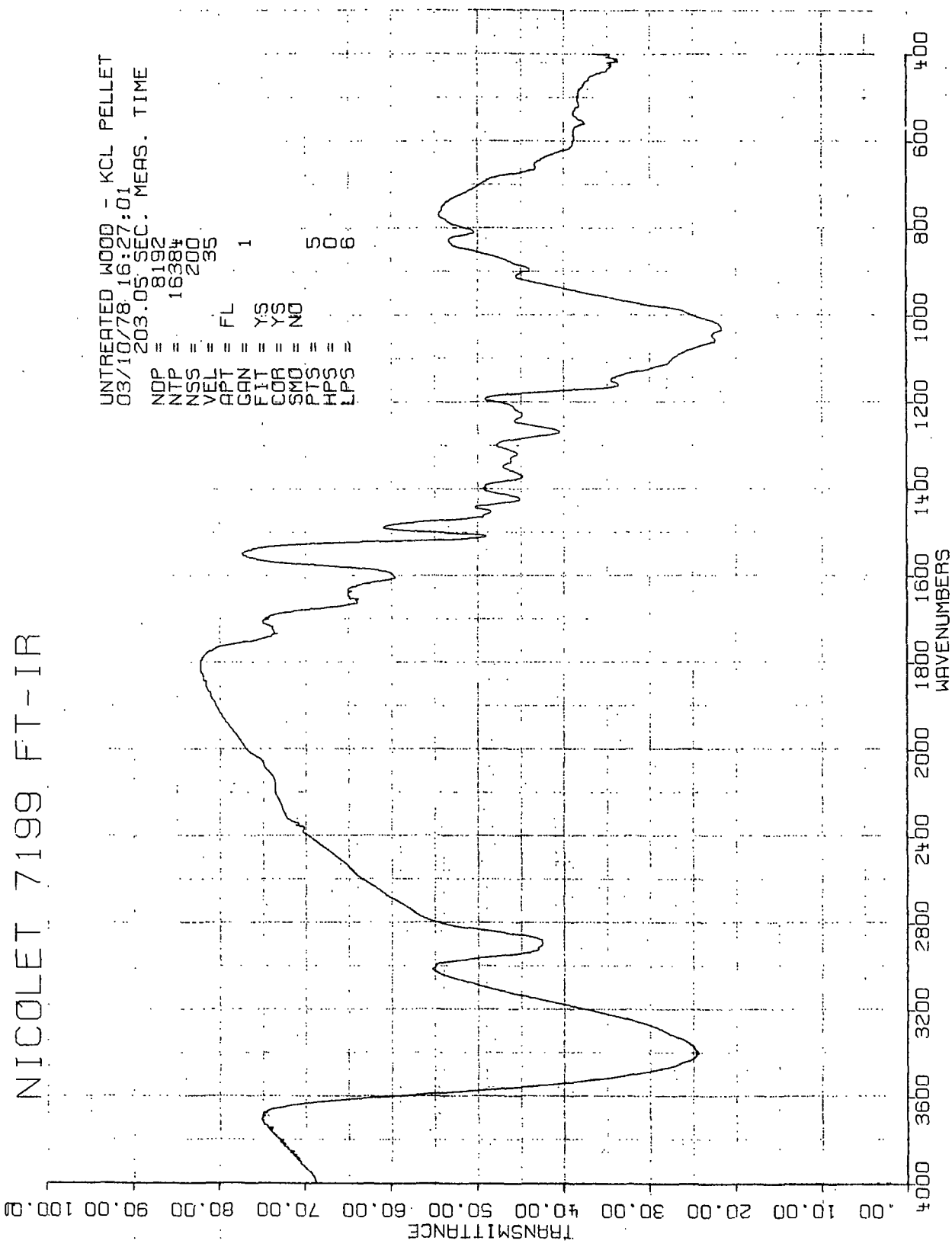

Figure 64. FT-IR Transmission Spectrum of Untreated FW

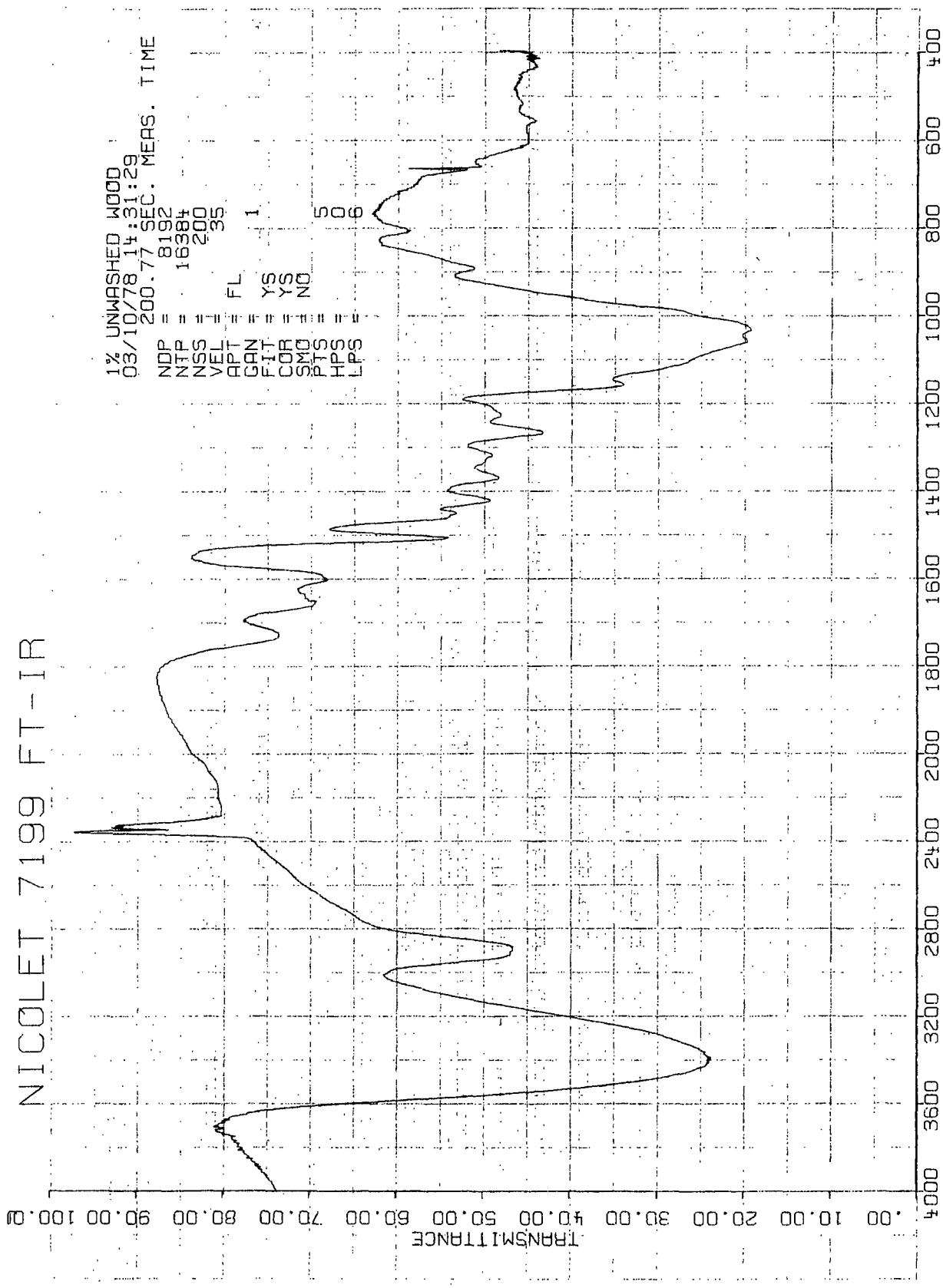

Figure 65. FT-IR Transmission Spectrum of 1% Ozonized, Unwashed FW

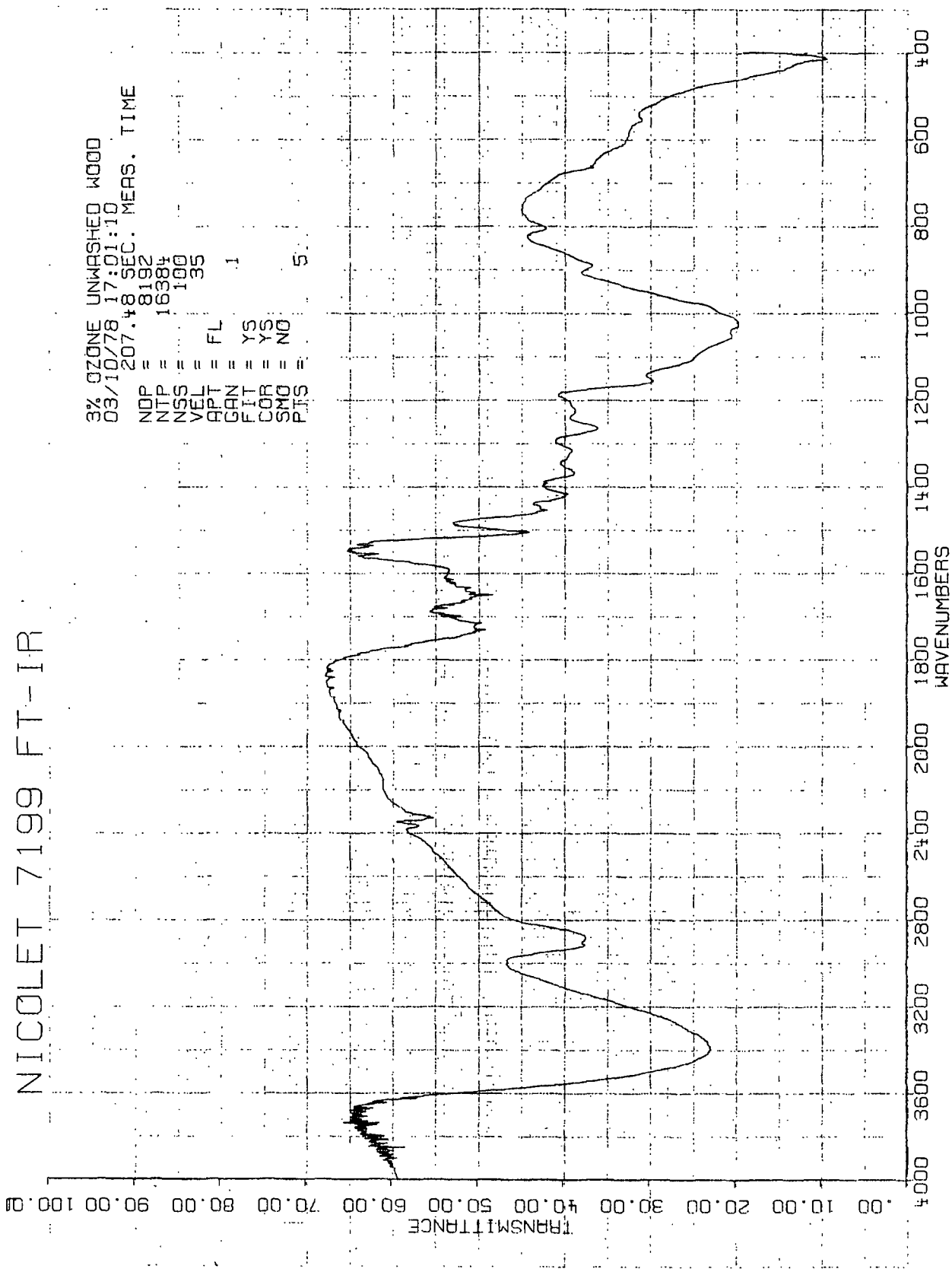

Figure 66. FT-IR Transmission Spectrum of 3% Ozonized, Unwashed FW

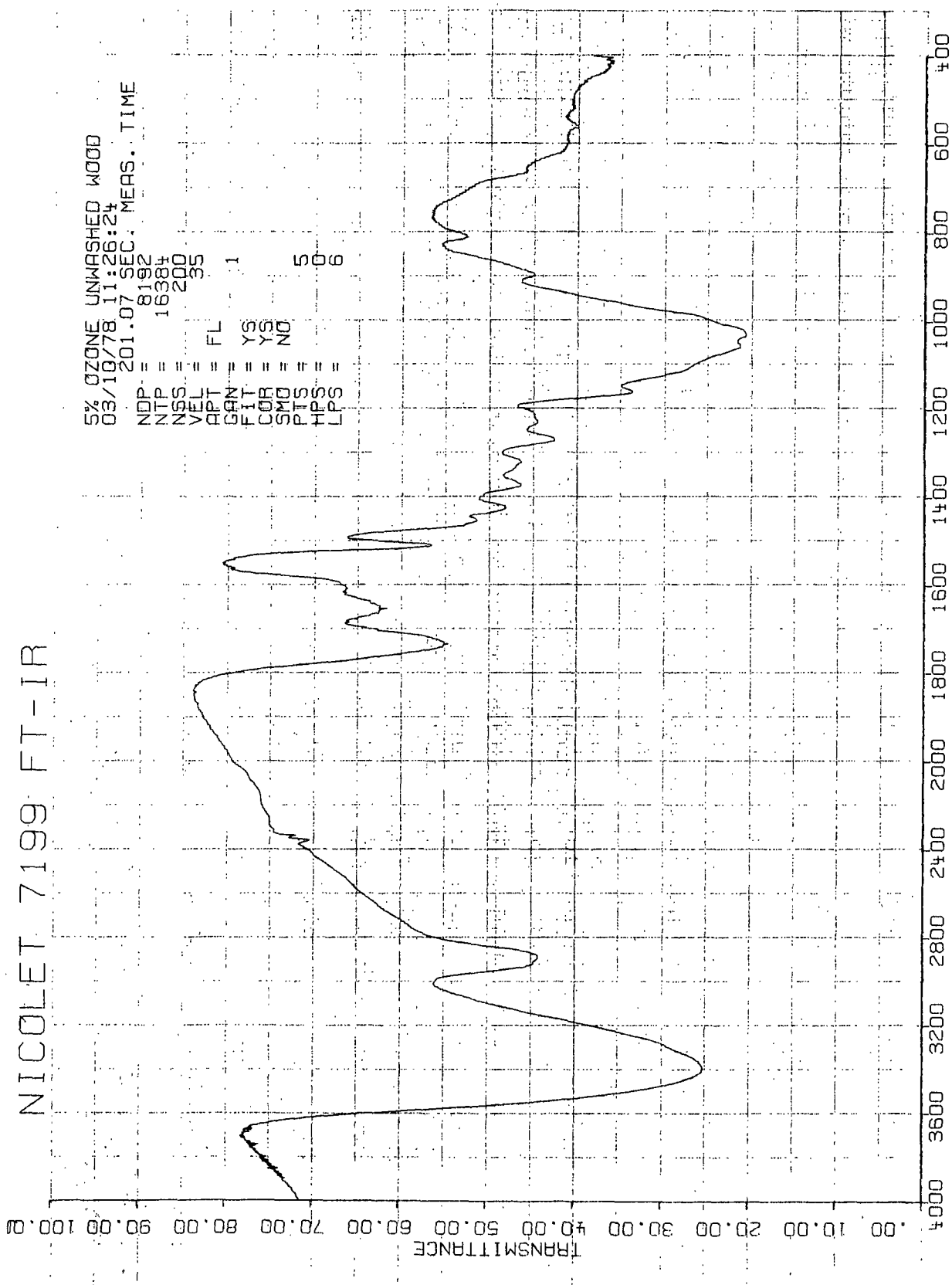

Figure 67. FT-IR Transmission Spectrum of 5% Ozonized, Unwashed FW

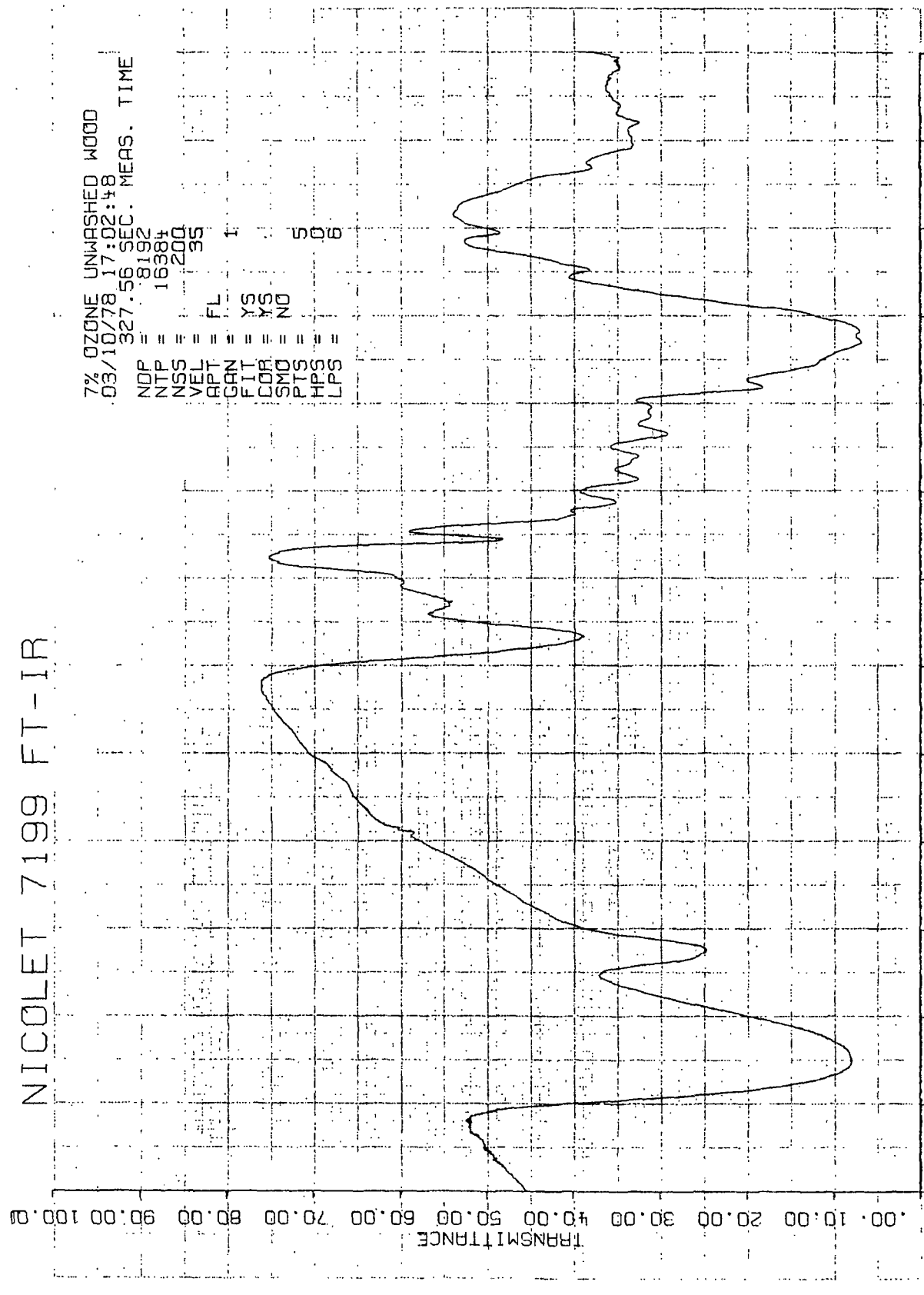

Figure 68. FT-IR Transmission Spectrum of 7% Ozonized, Unwashed FW

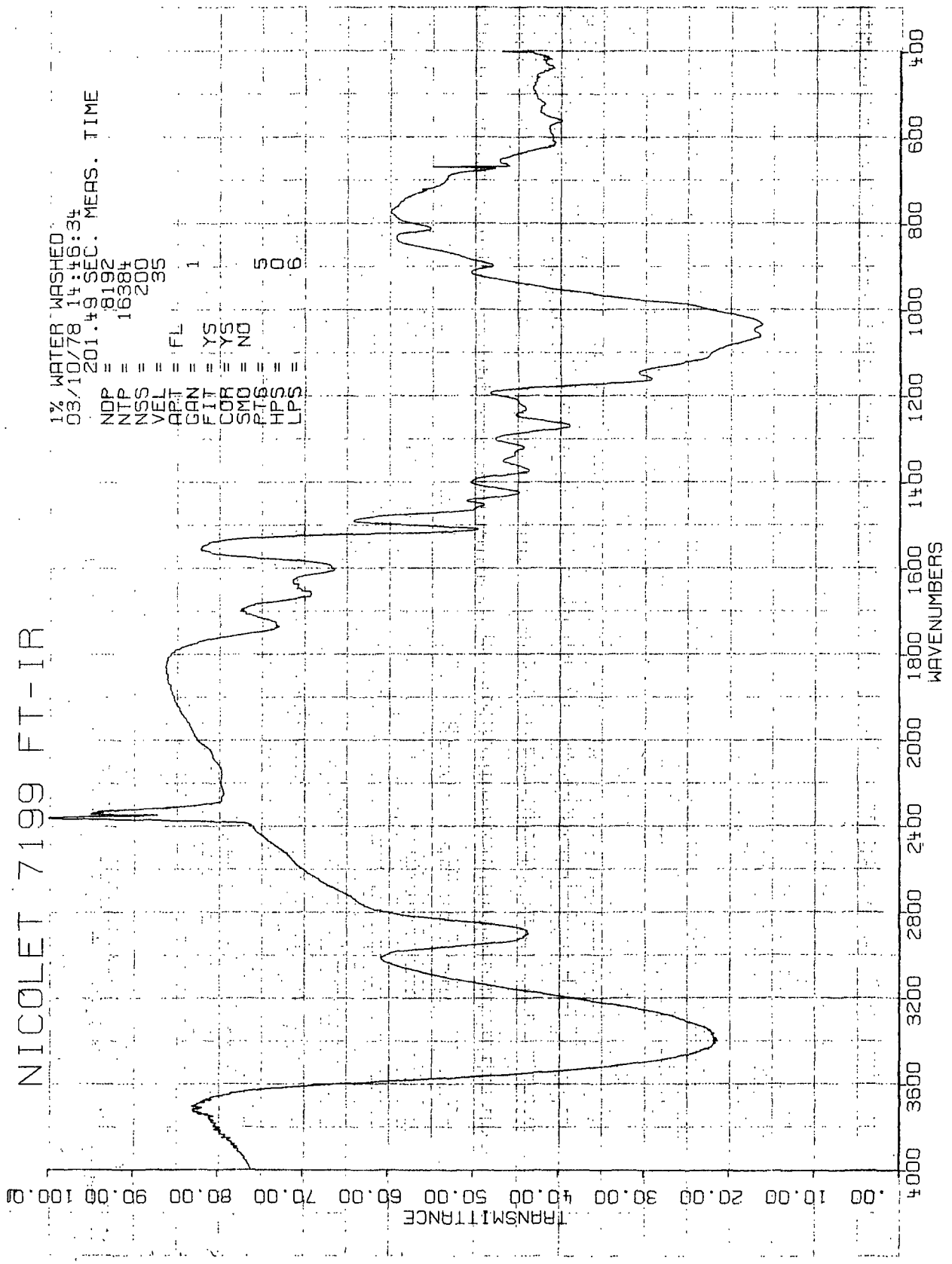

Figure 69. FT-IR Transmission Spectrum of 1% Ozonized, Washed FW

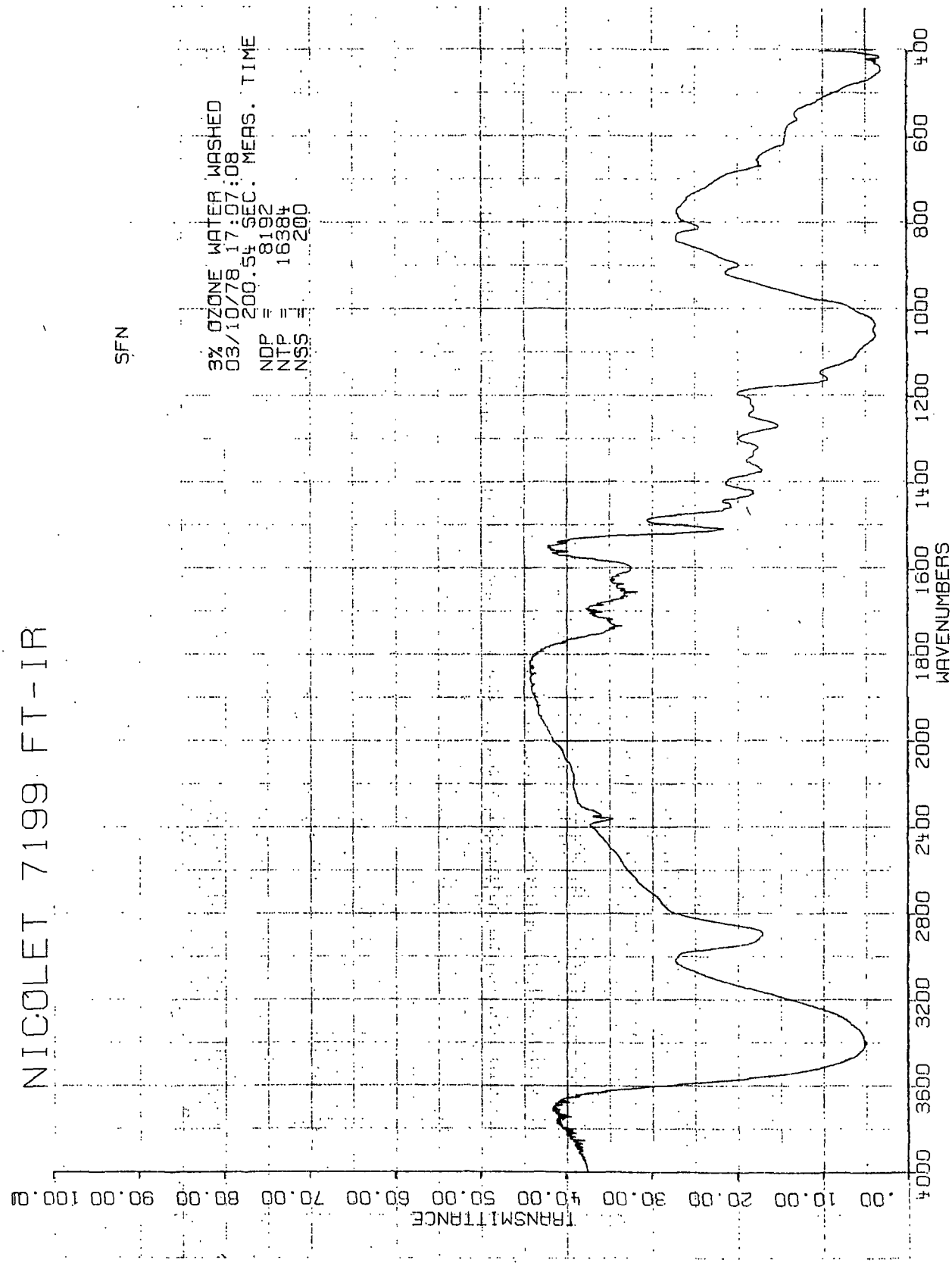

Figure 70. FT-IR Transmission Spectrum of 3% Ozonized, Washed FW

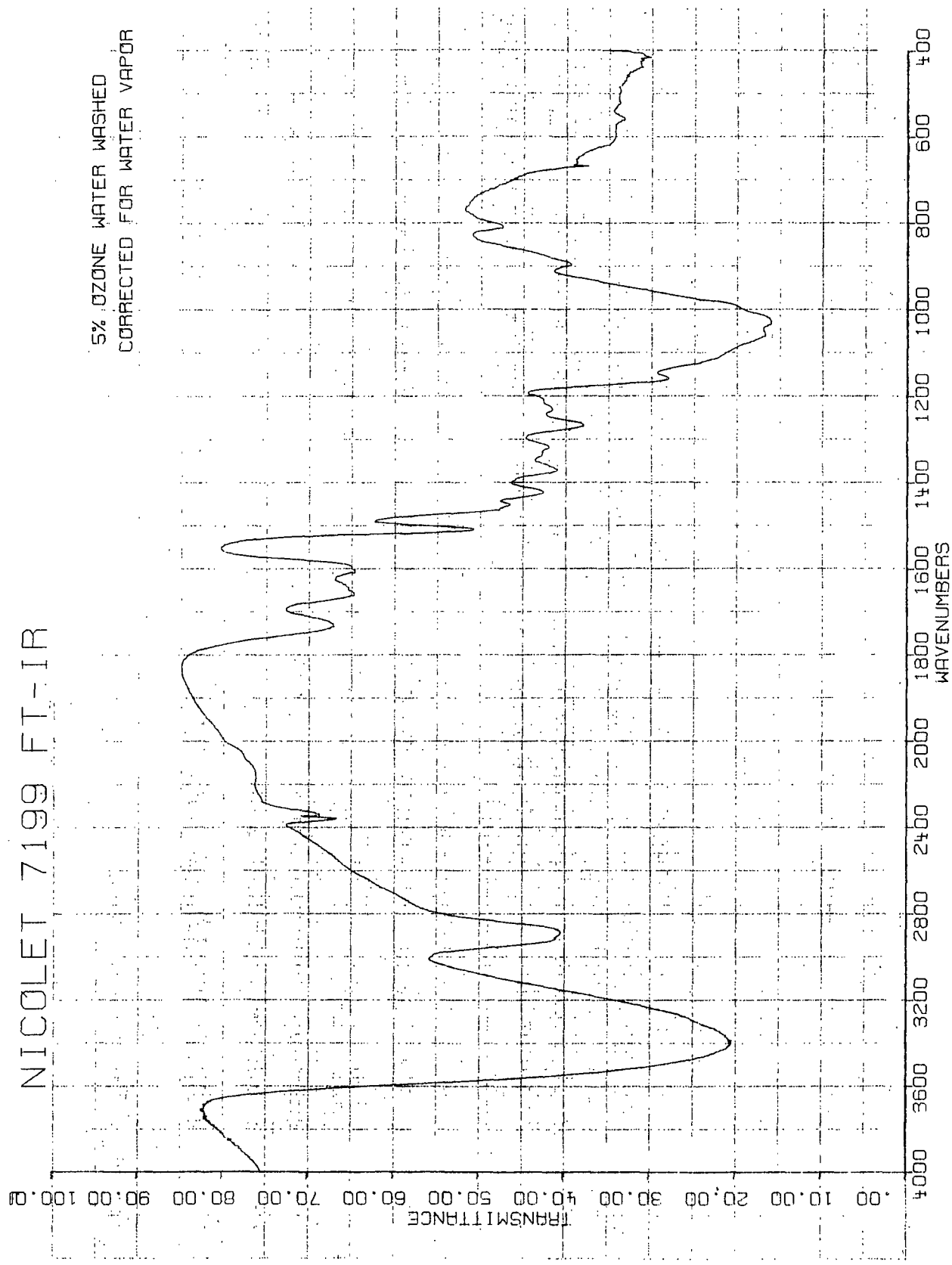

Figure 71. FT-IR Transmission Spectrum of 5% Ozonized, Washed FW

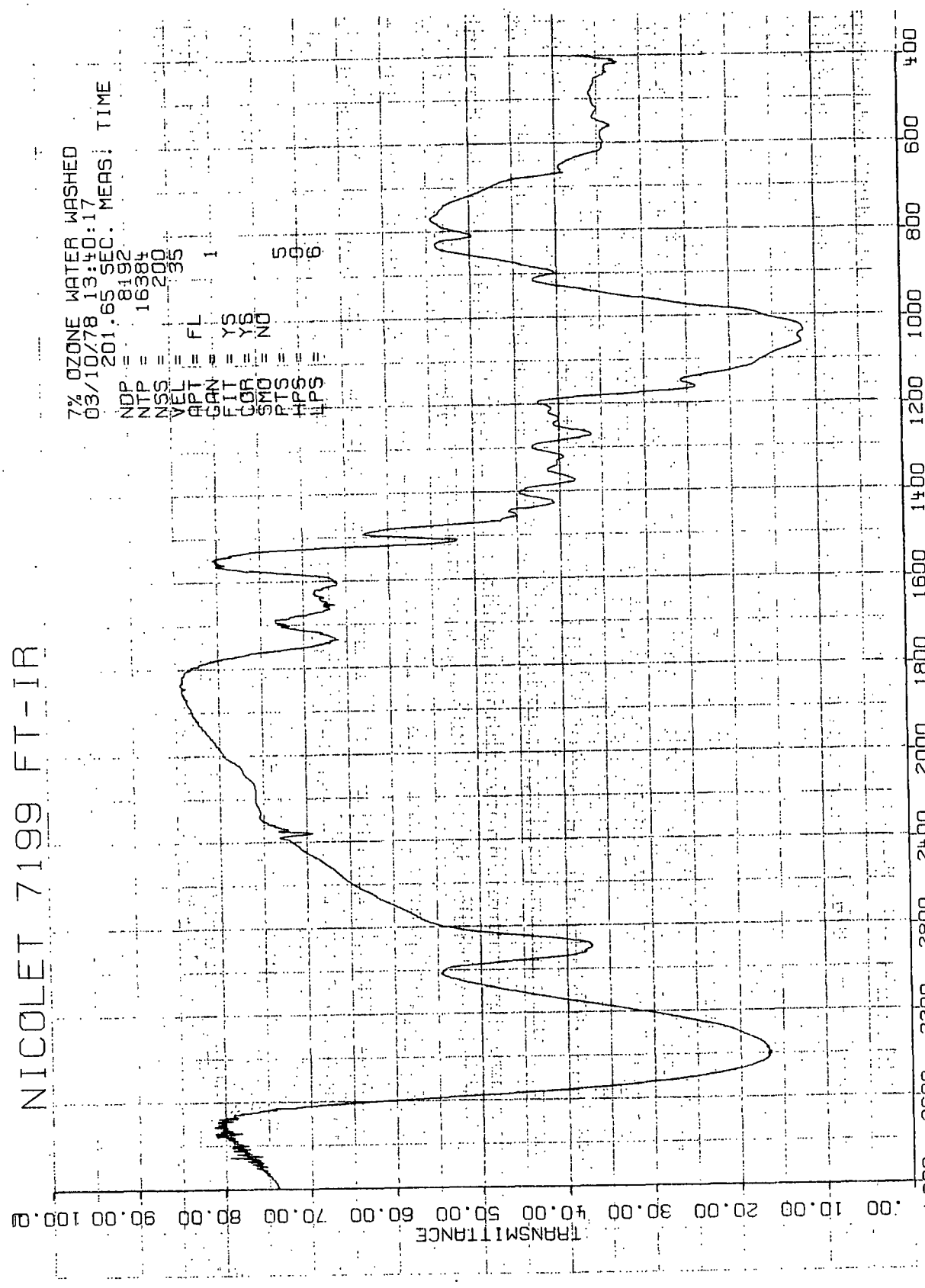

Figure 72. FT-IR Transmission Spectrum of 7% Ozonized, Washed FW

APPENDIX V

NEUTRALIZED FIBERIZED WOOD FT-IR TRANSMISSION SPECTRA

FT-IR transmission spectra were obtained for untreated and ozonated, washed FW samples. The samples had been neutralized to a pH = 9.2 (see Experimental section). The spectra are given in Fig. 73-77.

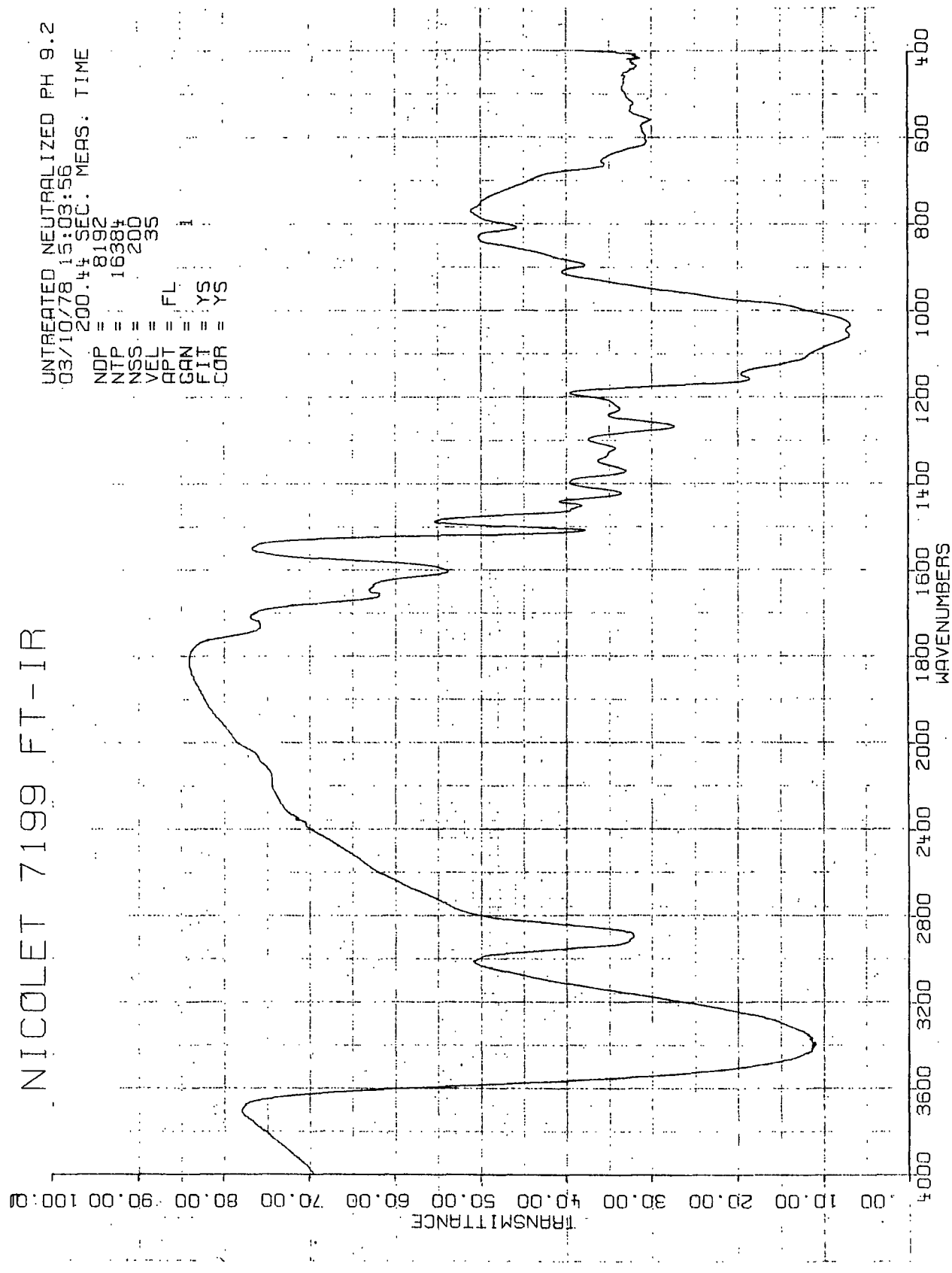

Figure 73. FT-IR Transmission Spectrum of Untreated, Neutralized FW

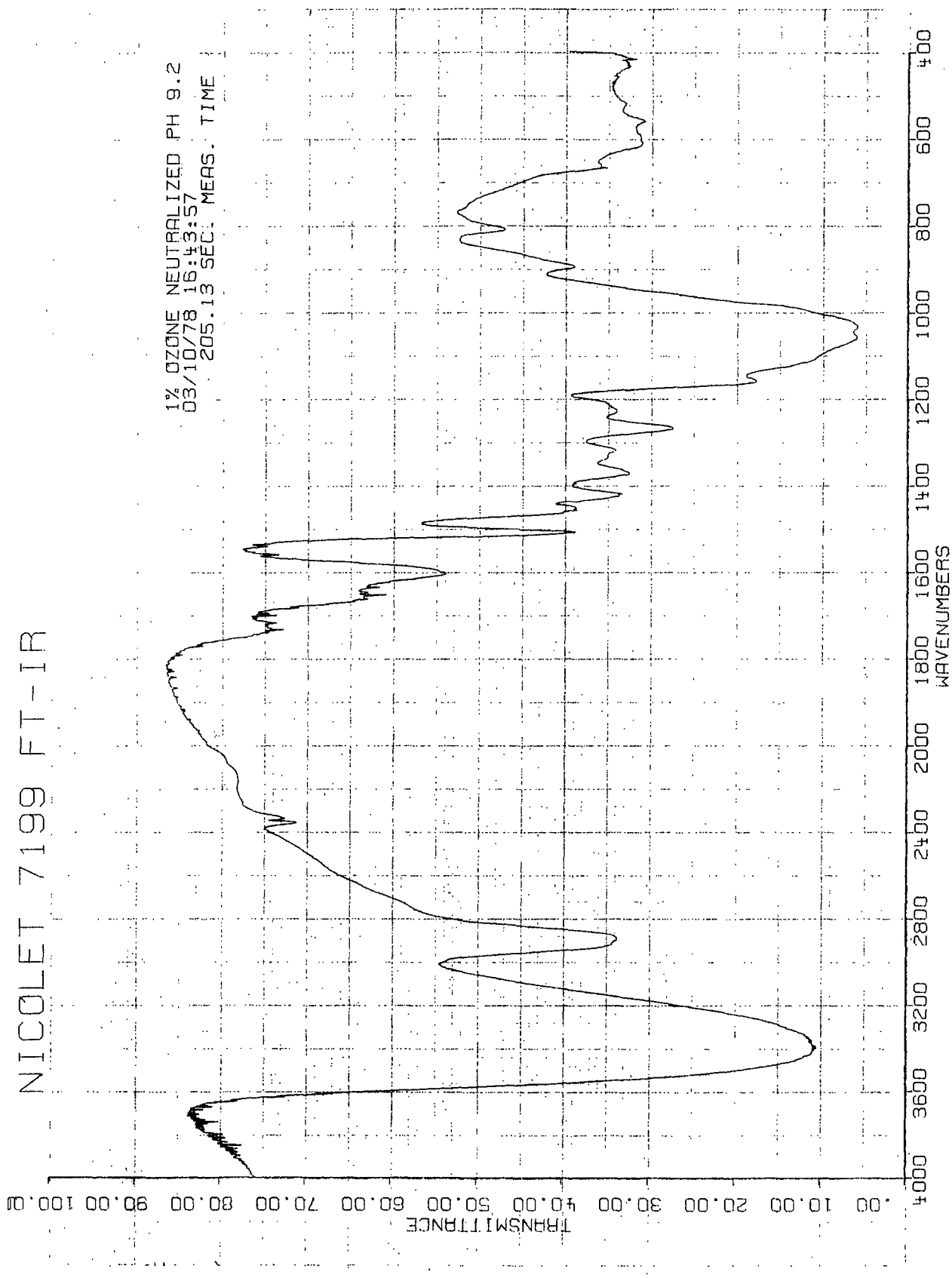

Figure 74. FT-IR Transmission Spectrum of 1% Ozonized, Washed, Neutralized FW

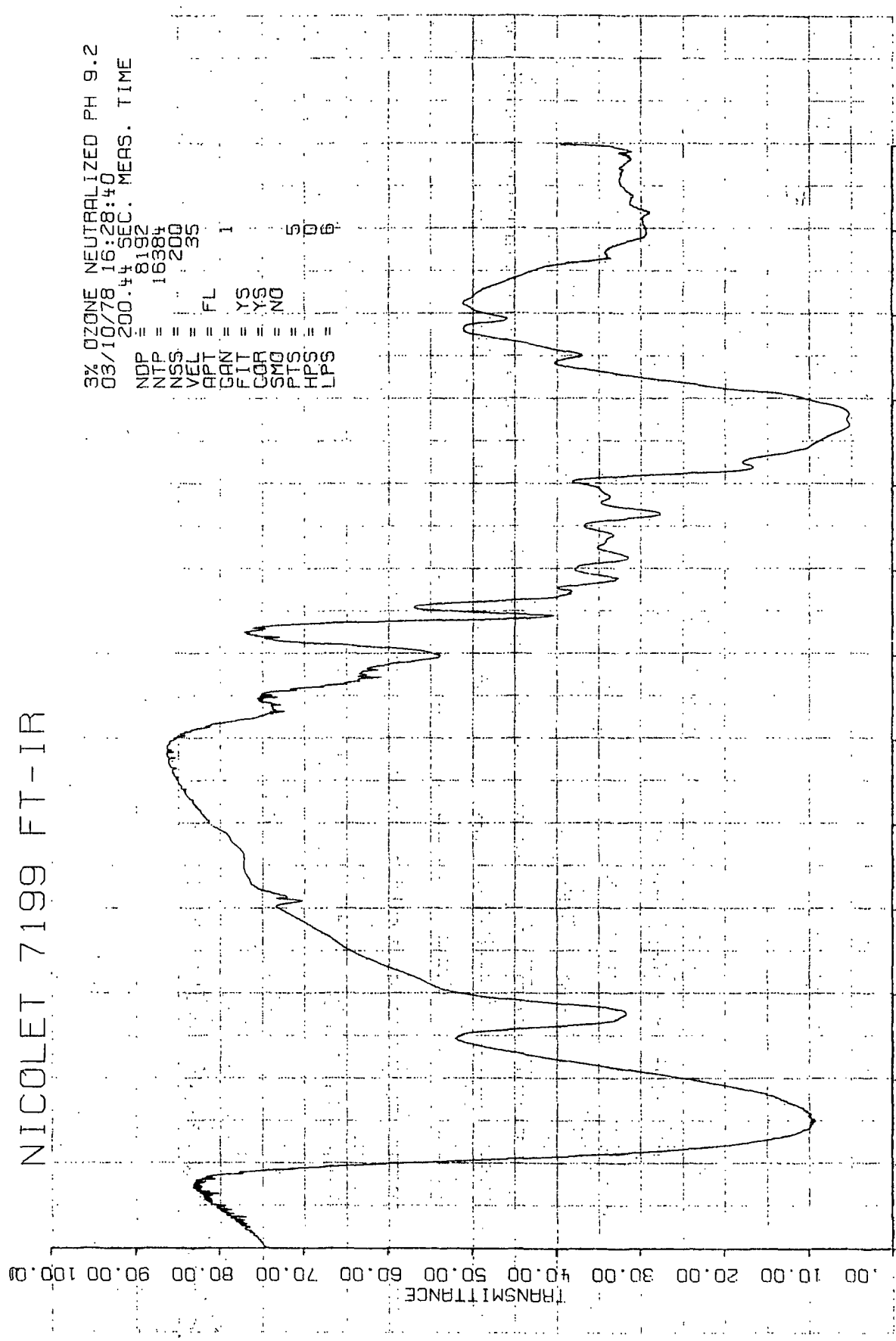

Figure 75. FT-IR Transmission Spectrum of 3% Ozonized, Washed, Neutralized FW

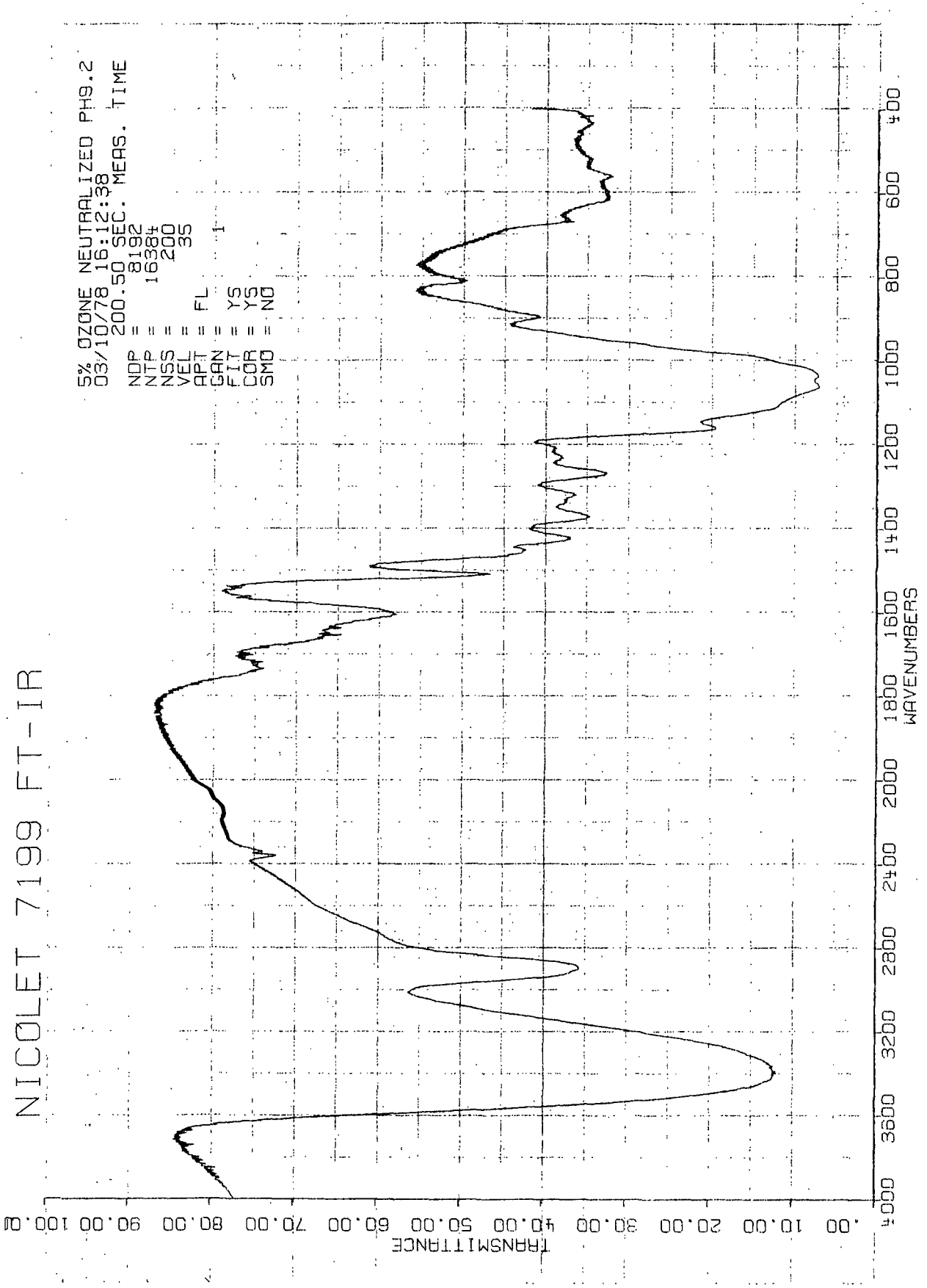

Figure 76. FT-IR Transmission Spectrum of 5% Ozonized, Washed, Neutralized FW

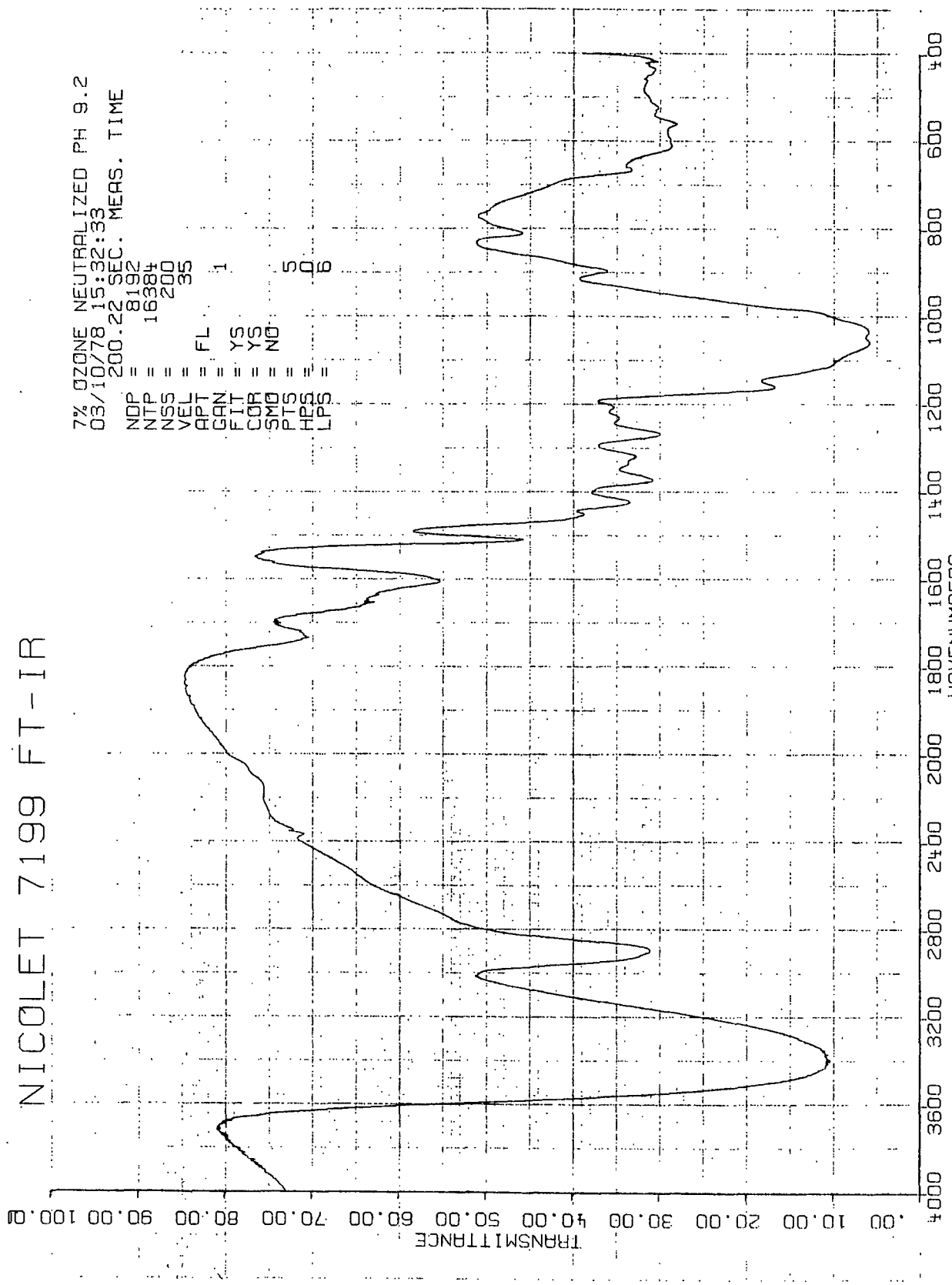

Figure 77. FT-IR Transmission Spectrum of 7% Ozonized, Washed, Neutralized FW

APPENDIX VI

ACIDIFIED FIBERIZED WOOD FT-IR TRANSMISSION SPECTRA

FT-IR transmission spectra were obtained for untreated and ozonated, washed FW samples. The samples had been acidified to a pH = 2.1 (see Experimental section). The spectra are given in Fig. 78-82.

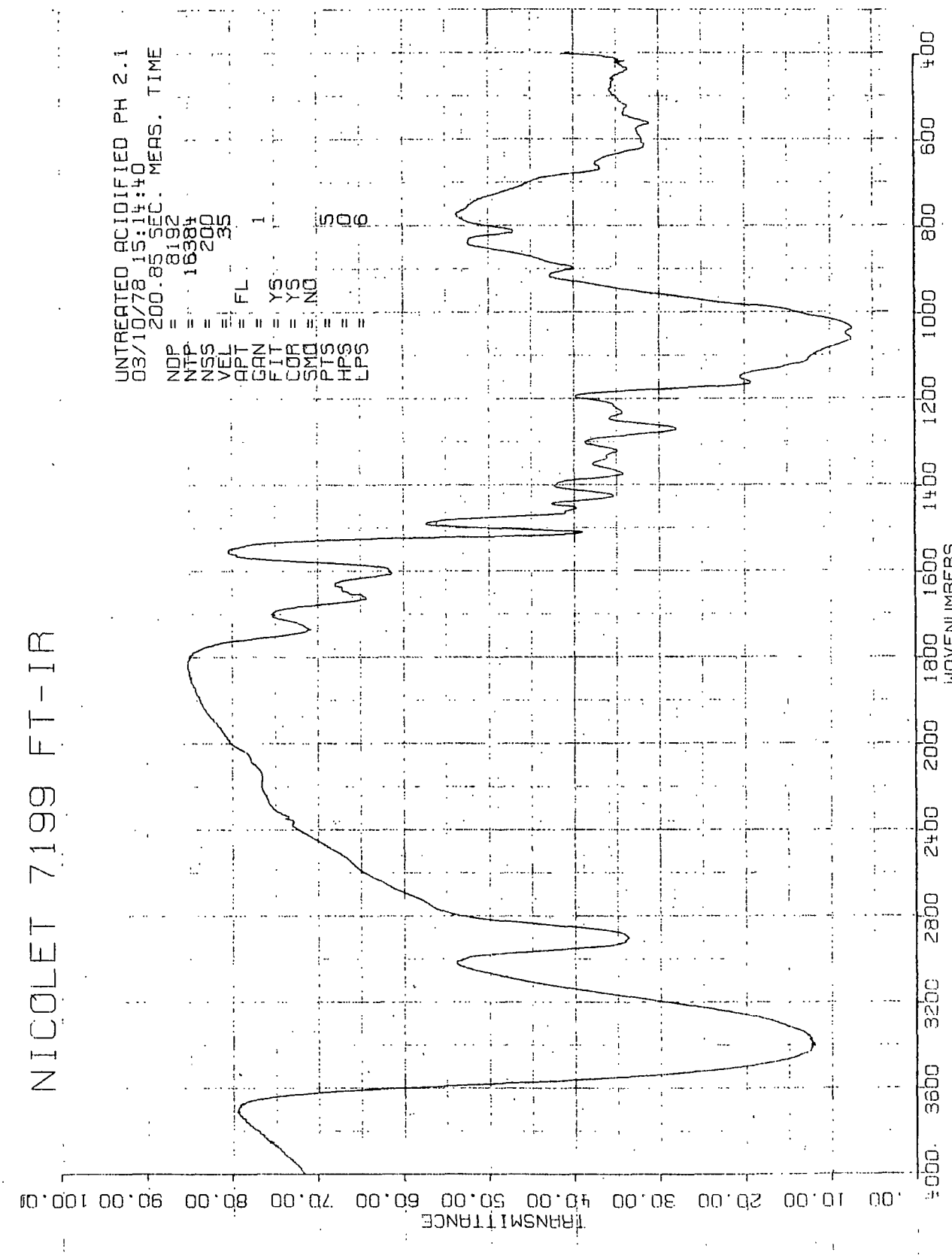

Figure 78. FT-IR Transmission Spectrum of Untreated, Acidified FW

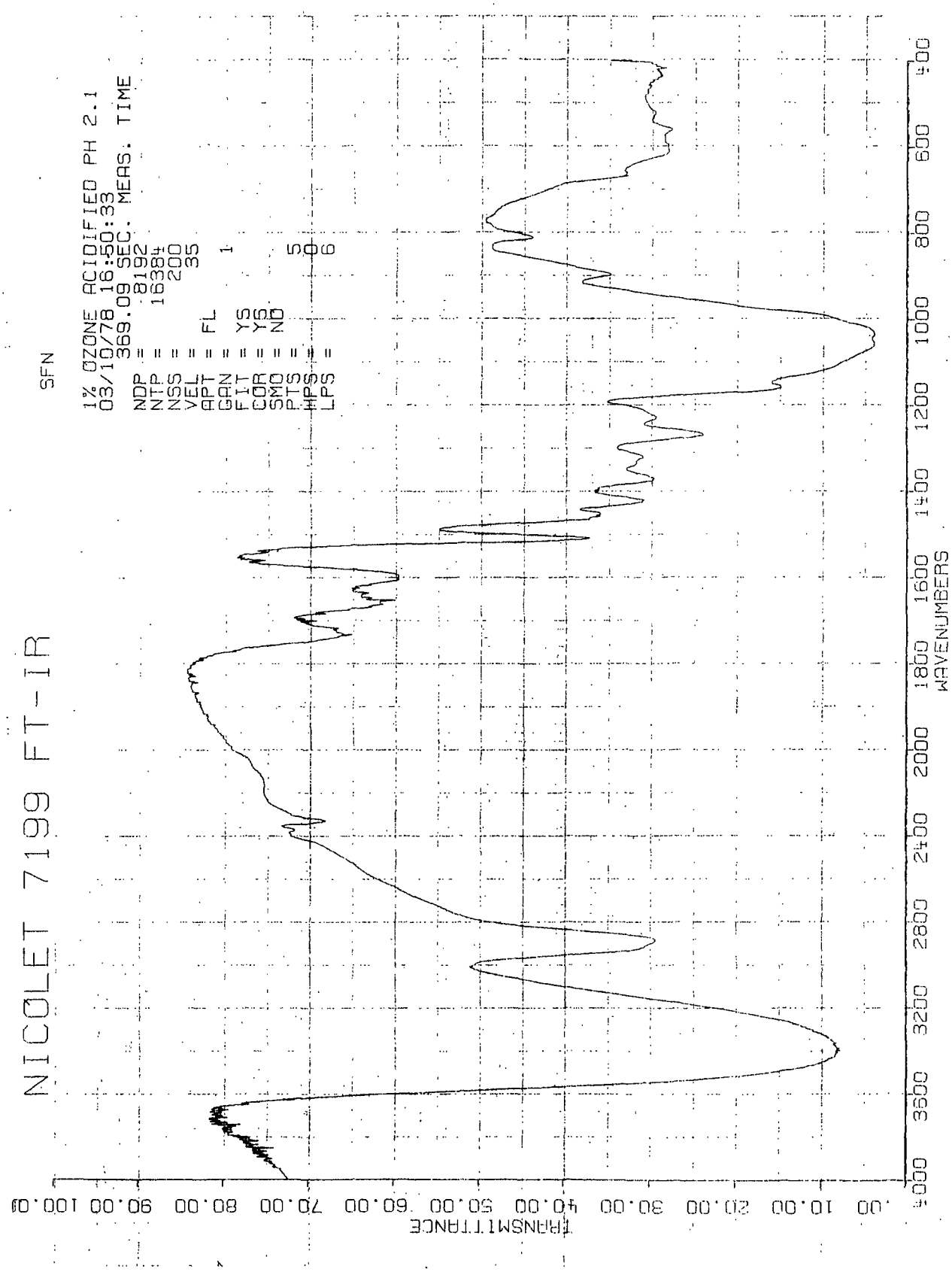

Figure 79. FT-IR Transmission Spectrum of 1% Ozonized, Washed, Acidified FW

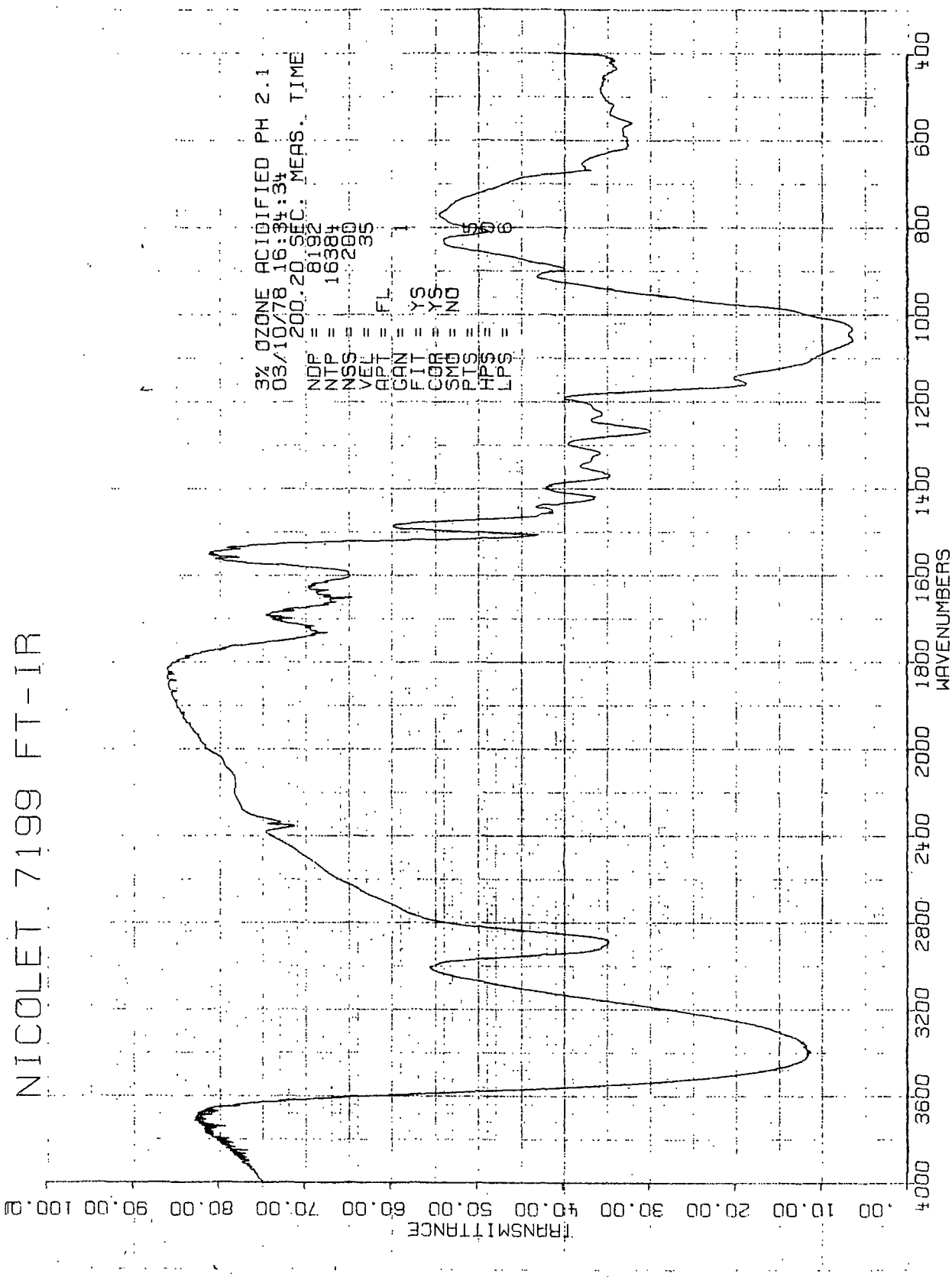

Figure 80. FT-IR Transmission Spectrum of 3% Ozonized, Washed, Neutralized FW

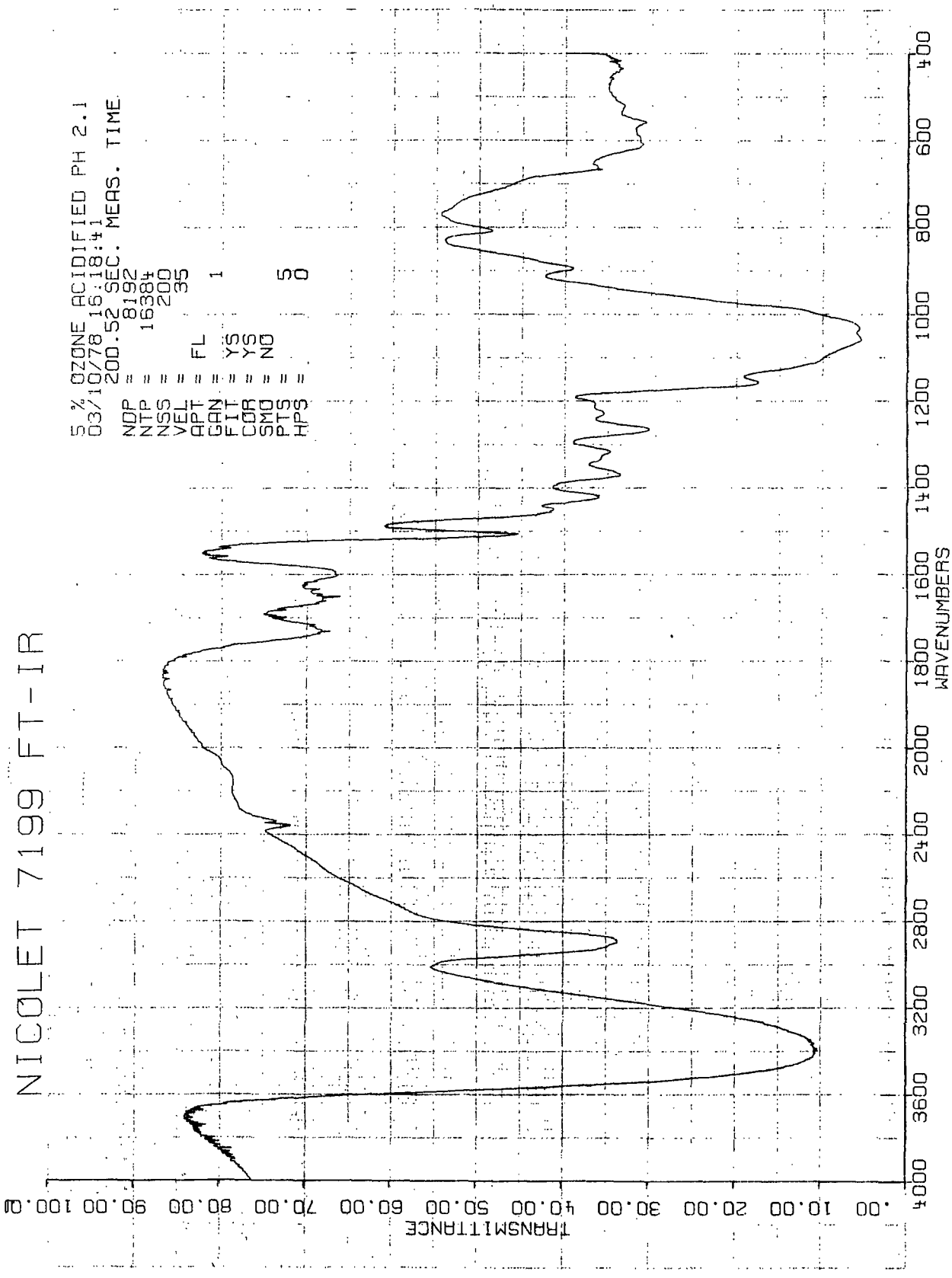

Figure 81. FT-IR Transmission Spectrum of 5% Ozonized, Washed, Acidified FW

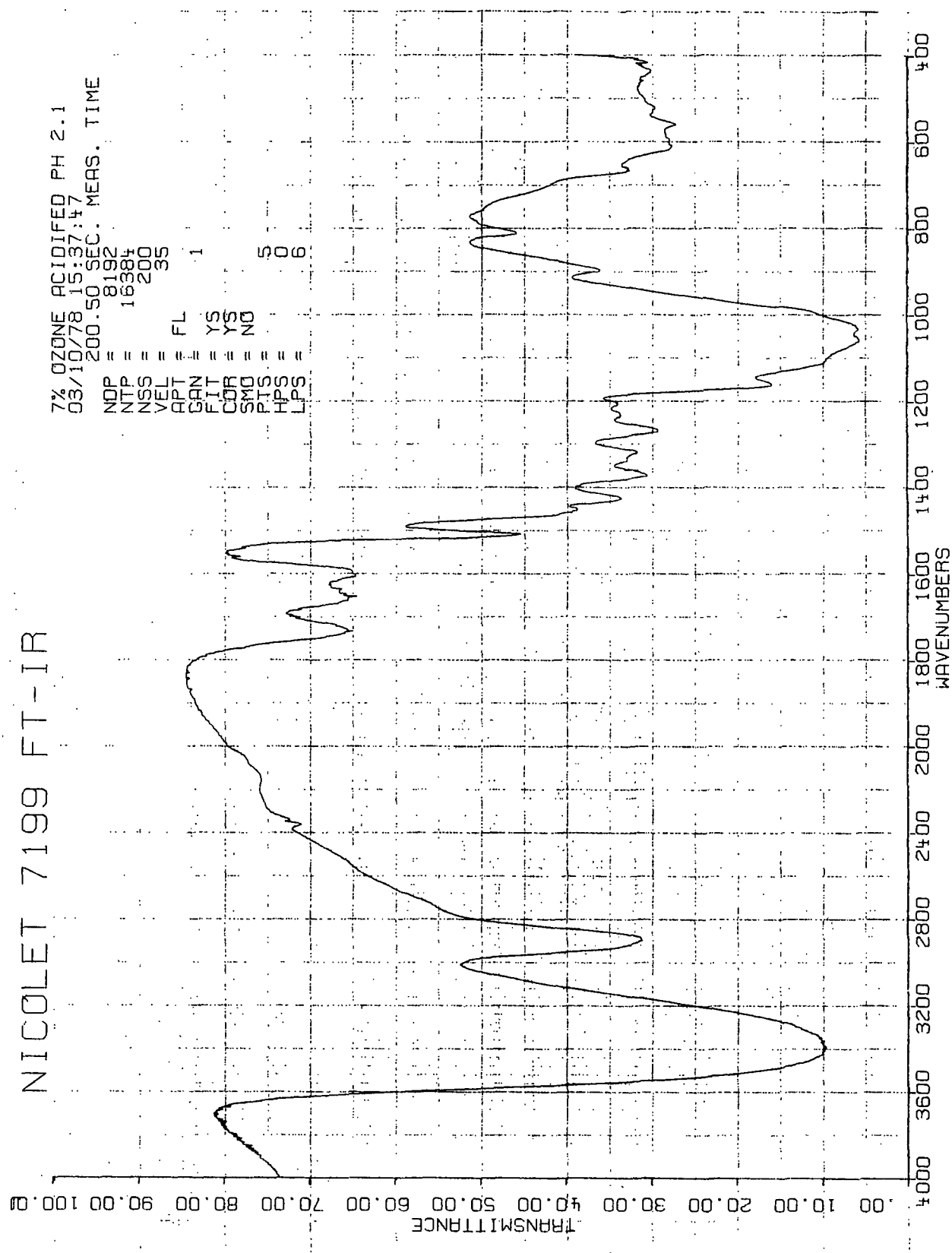

Figure 82. FT-IR Transmission Spectrum of 7% Ozonized, Washed, Acidified FW

APPENDIX VII

OZONATED FIBERIZED WOOD FT-IR DIFFERENCE SPECTRA

The following sets of FT-IR difference spectra were obtained, based on the transmission spectra given in Appendix IV:

1. Ozonated, unwashed FW minus untreated FW (Fig. 83-86)
2. Ozonated, washed FW minus untreated FW (Fig. 87-90)
3. Ozonated, unwashed FW minus ozonated, washed FW (Fig. 91-94)

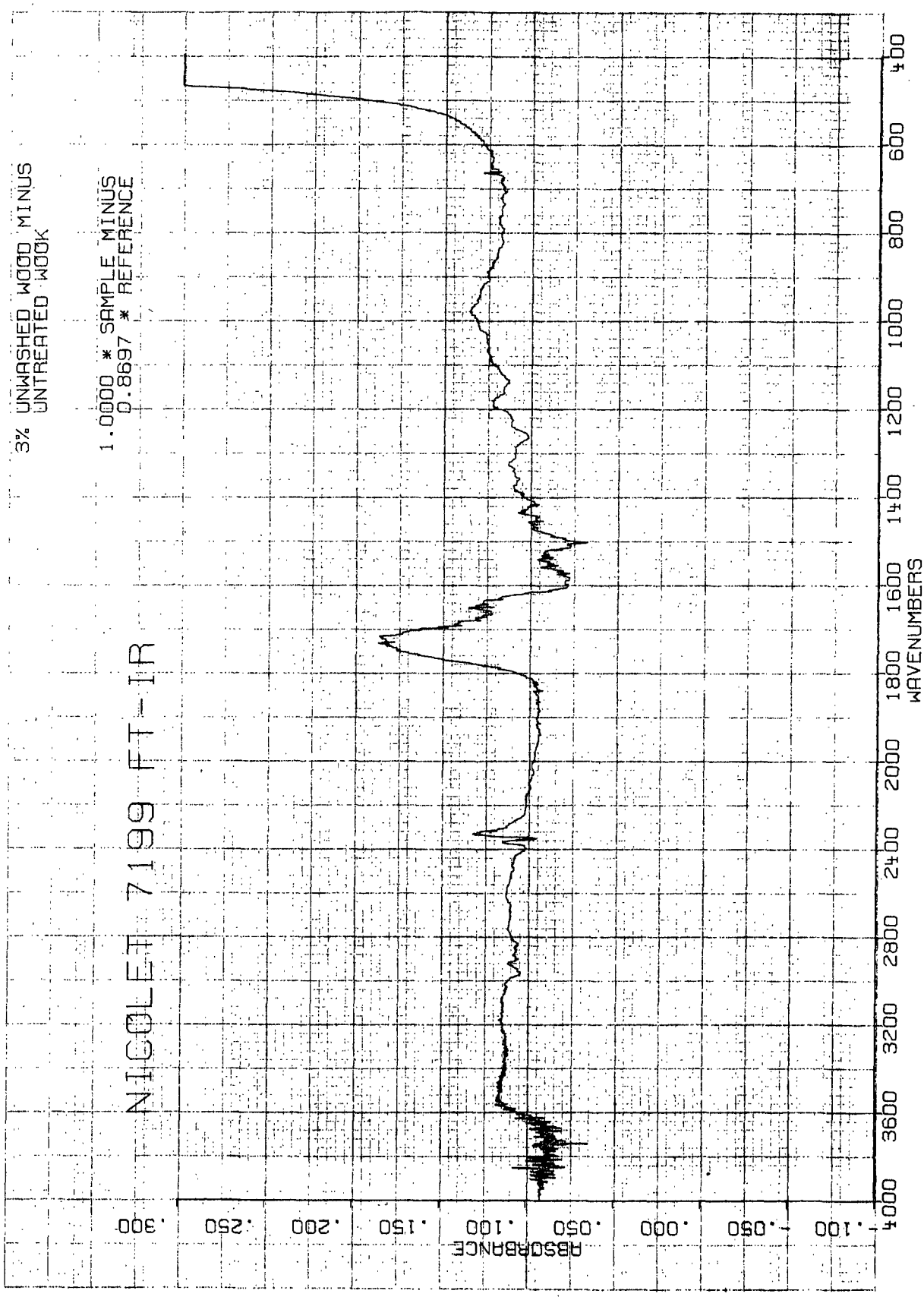

Figure 84. FT-IR Difference Spectrum of 3% Ozonized, Unwashed FW minus Untreated FW

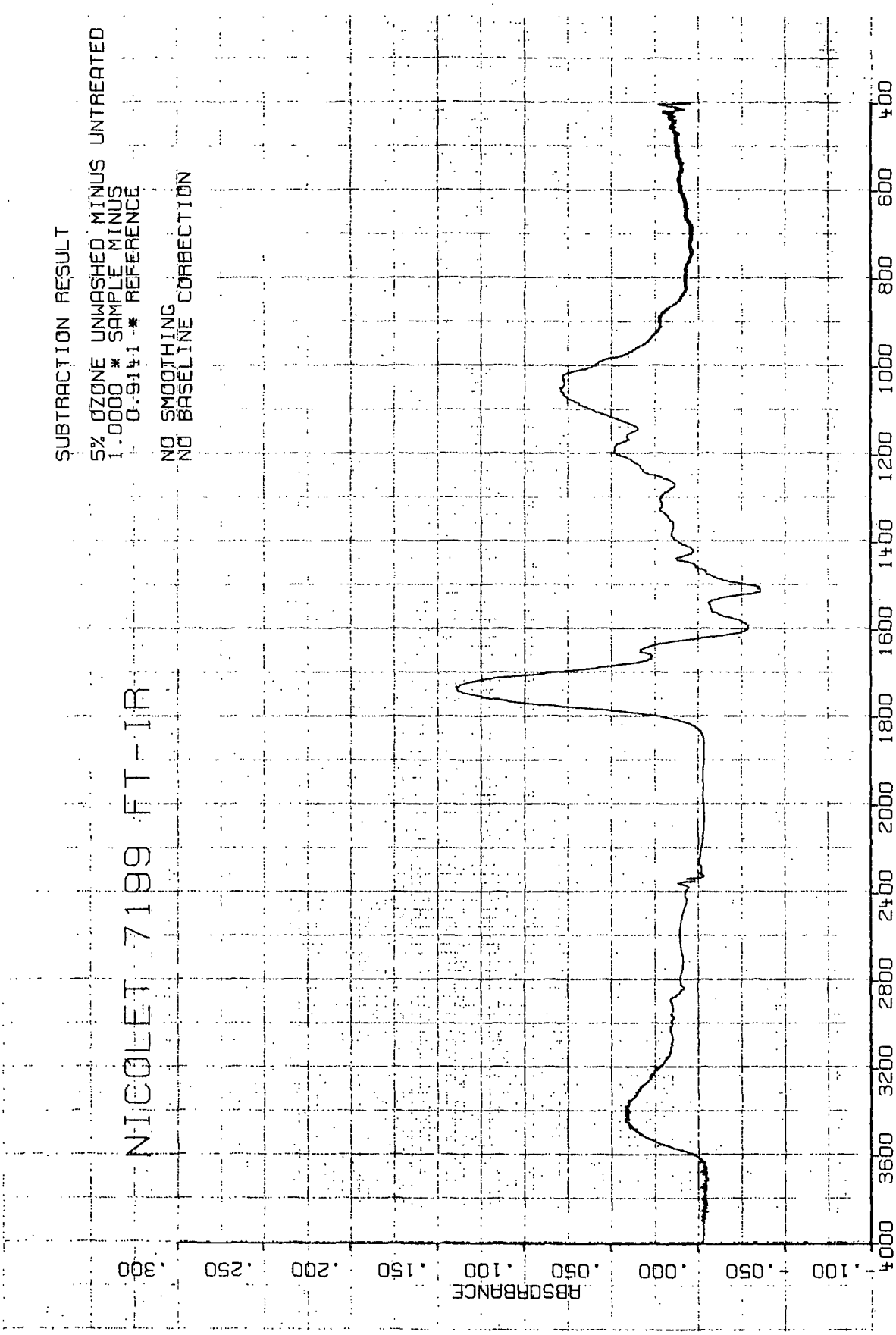

Figure 85. FT-IR Difference Spectrum of 5% Ozonized, Unwashed FW minus Untreated FW

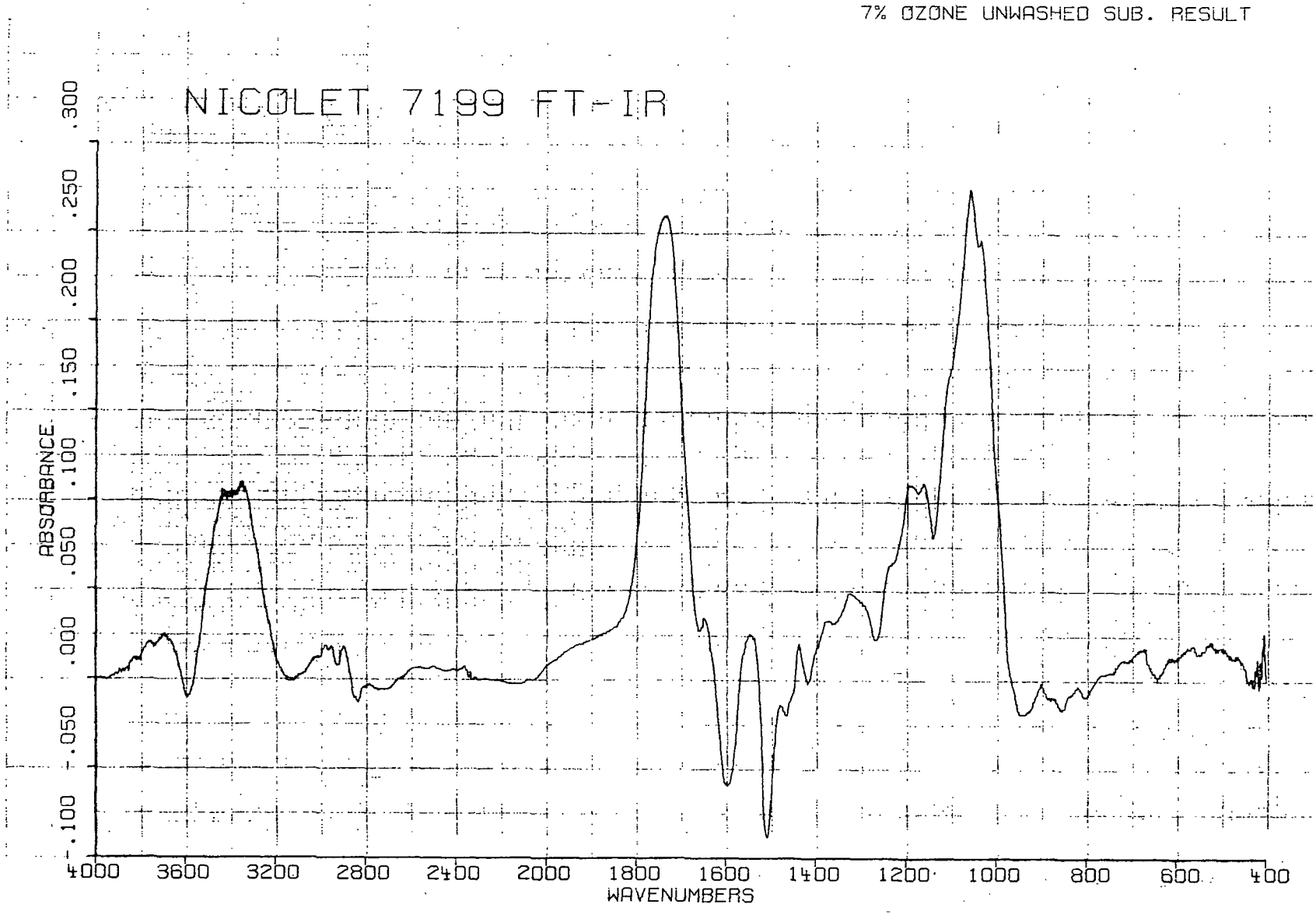

Figure 86. FT-IR Difference Spectrum of 7% Ozonized, Unwashed FW minus Untreated FW

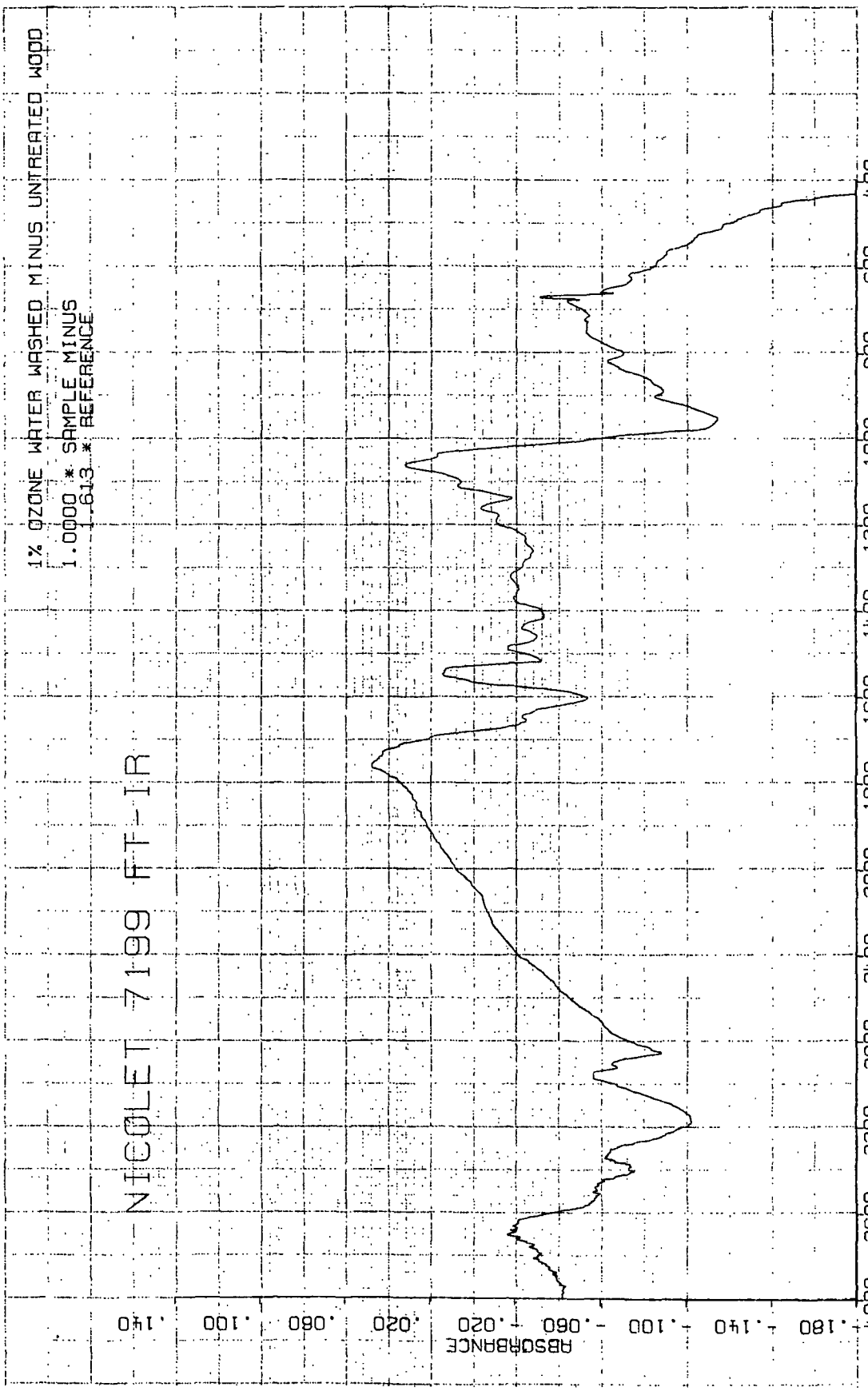

Figure 87. FT-IR Difference Spectrum of 1% Ozonized, Washed FW minus Uhtreated FW

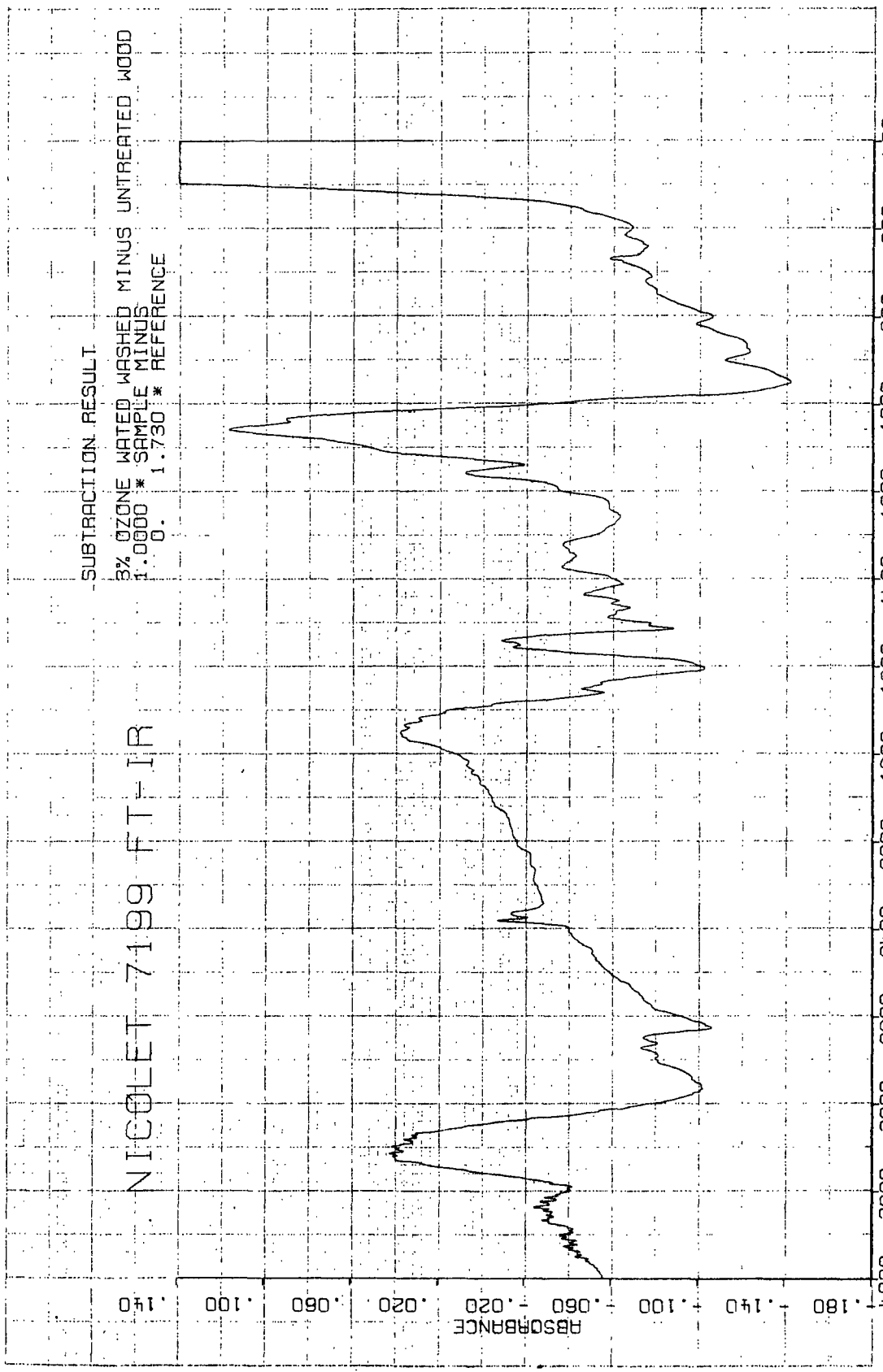

Figure 88. FT-IR Difference Spectrum of 3% Ozonized, Washed FW minus Untreated FW

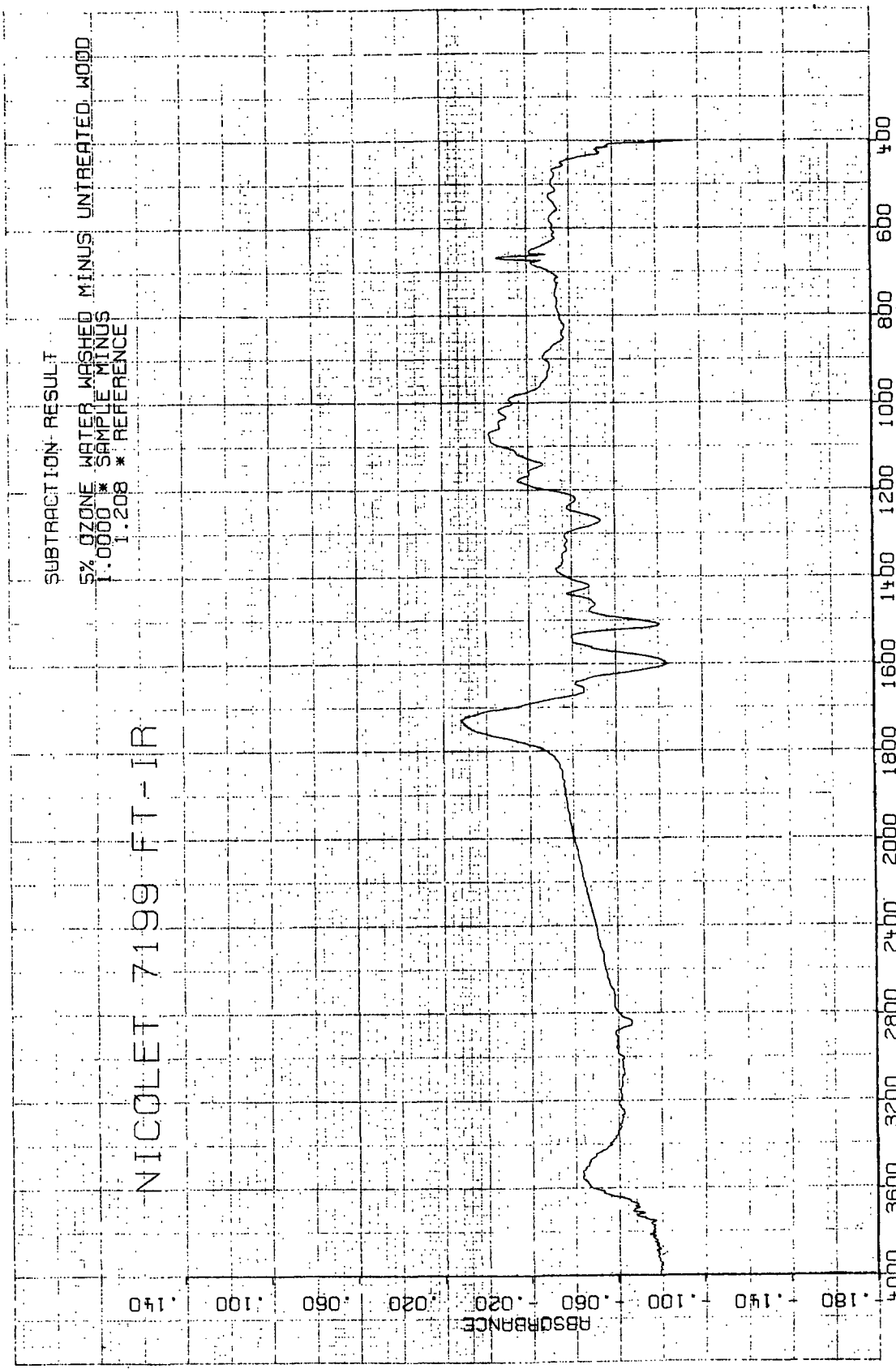

Figure 89. FT-IR Difference Spectrum of 5% Ozonized, Washed FW minus Untreated FW

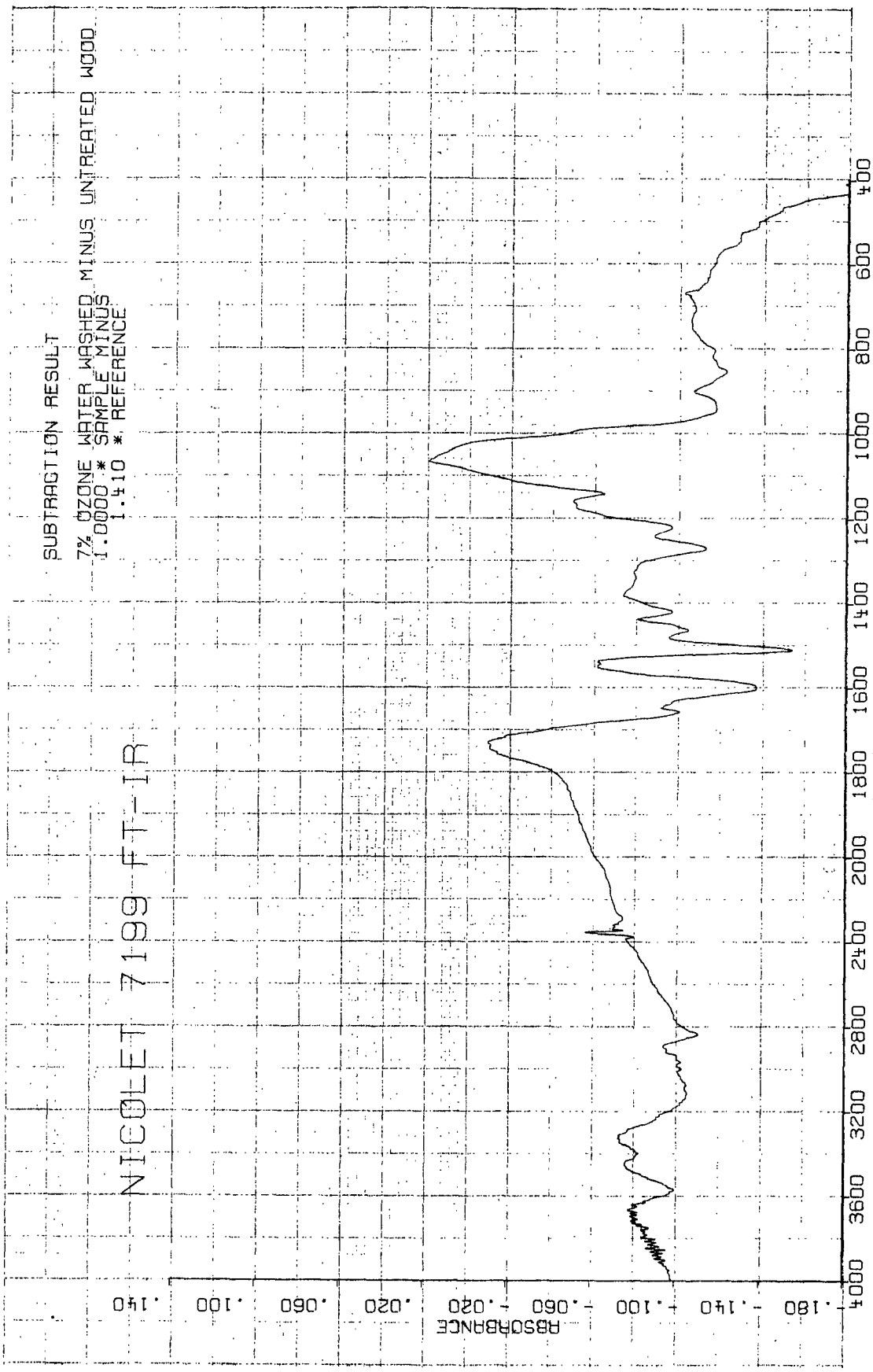

Figure 90. FT-IR Difference Spectrum of 7% Ozonized, Washed FW minus Untreated FW

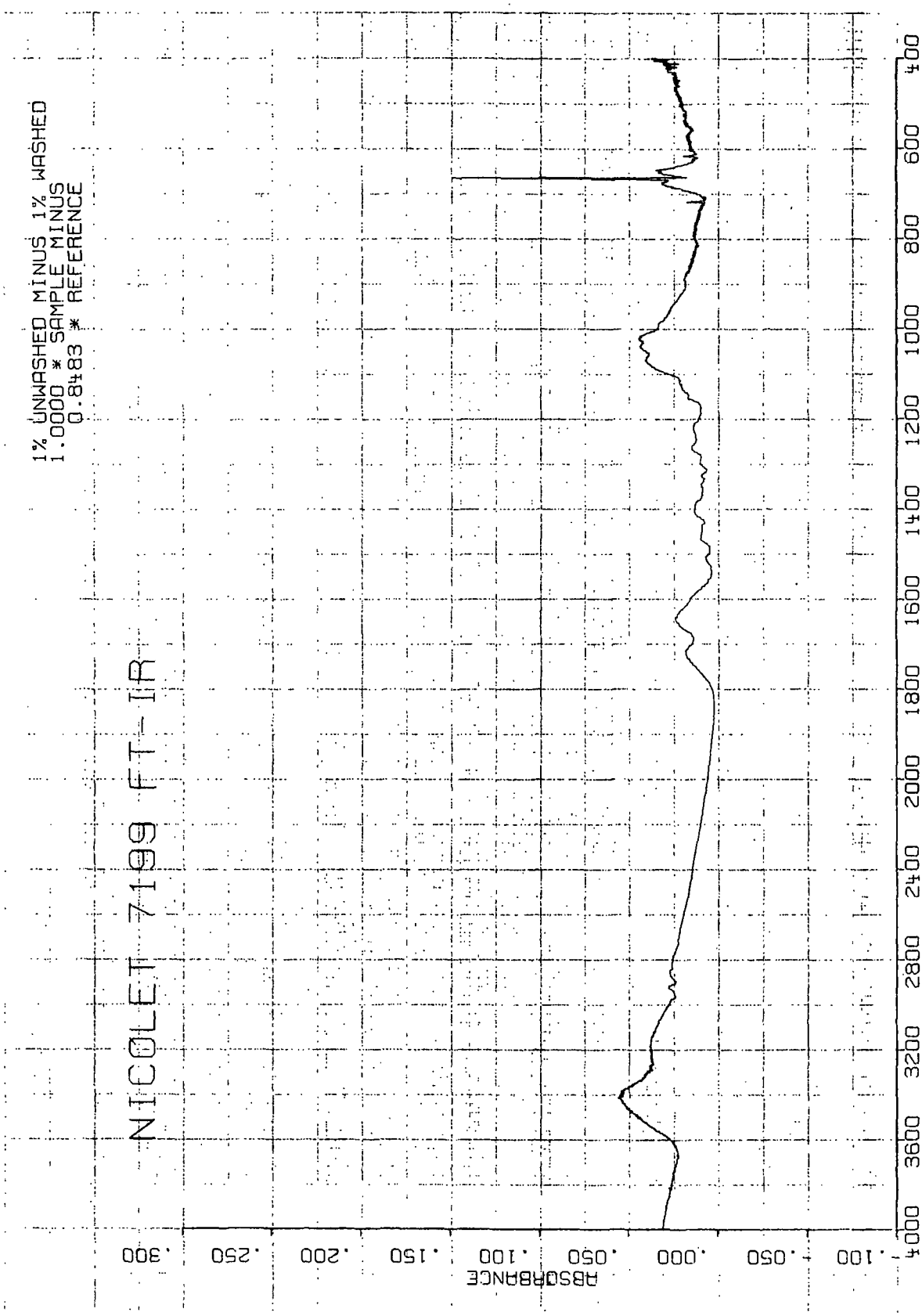

Figure 91. FT-IR Difference Spectrum of 1% Ozonized, Unwashed FW minus 1% Ozonized, Washed FW

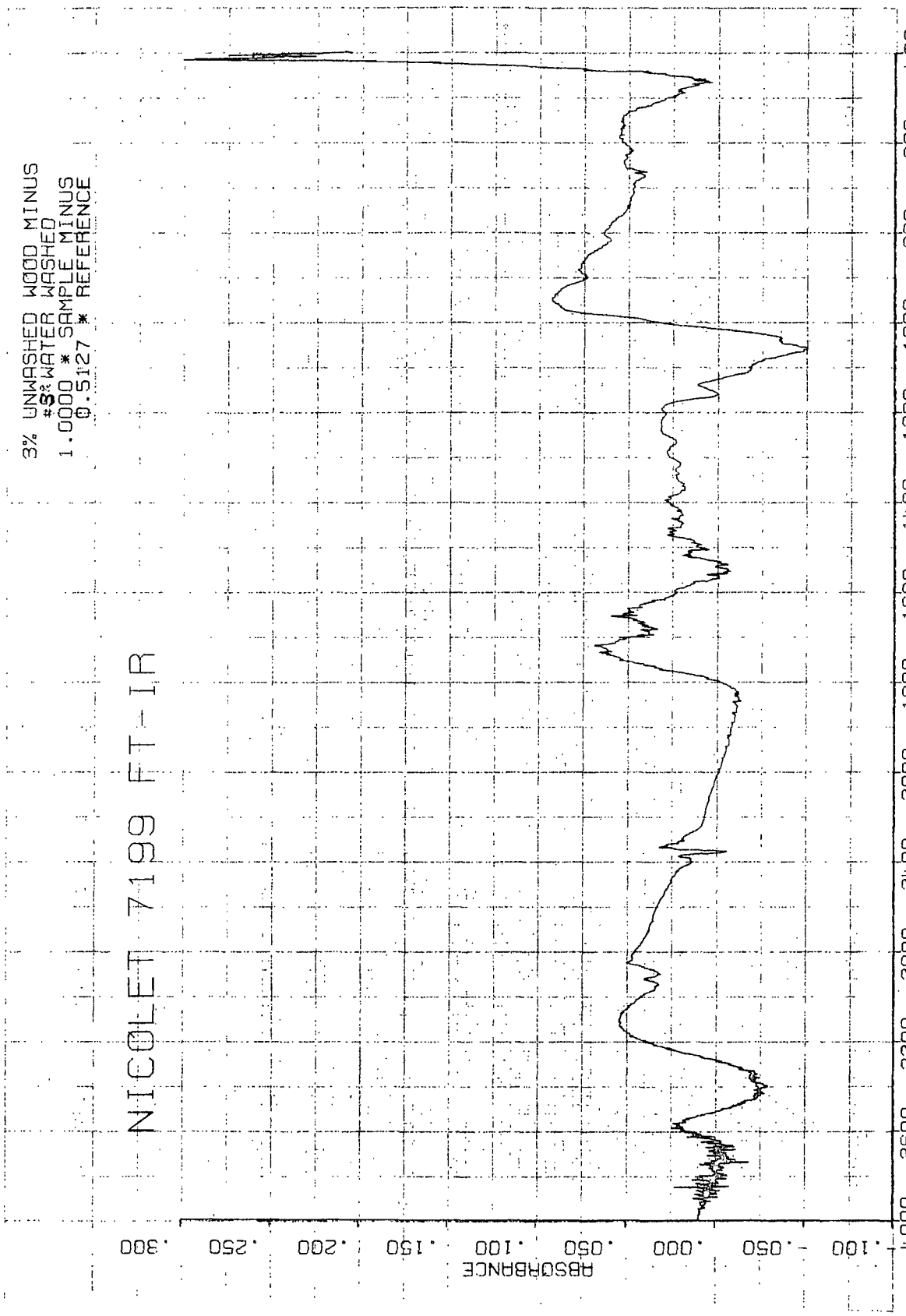

Figure 92. FT-IR Difference Spectrum of 3% Ozonized, Unwashed FW minus 3% Ozonized, Washed FW

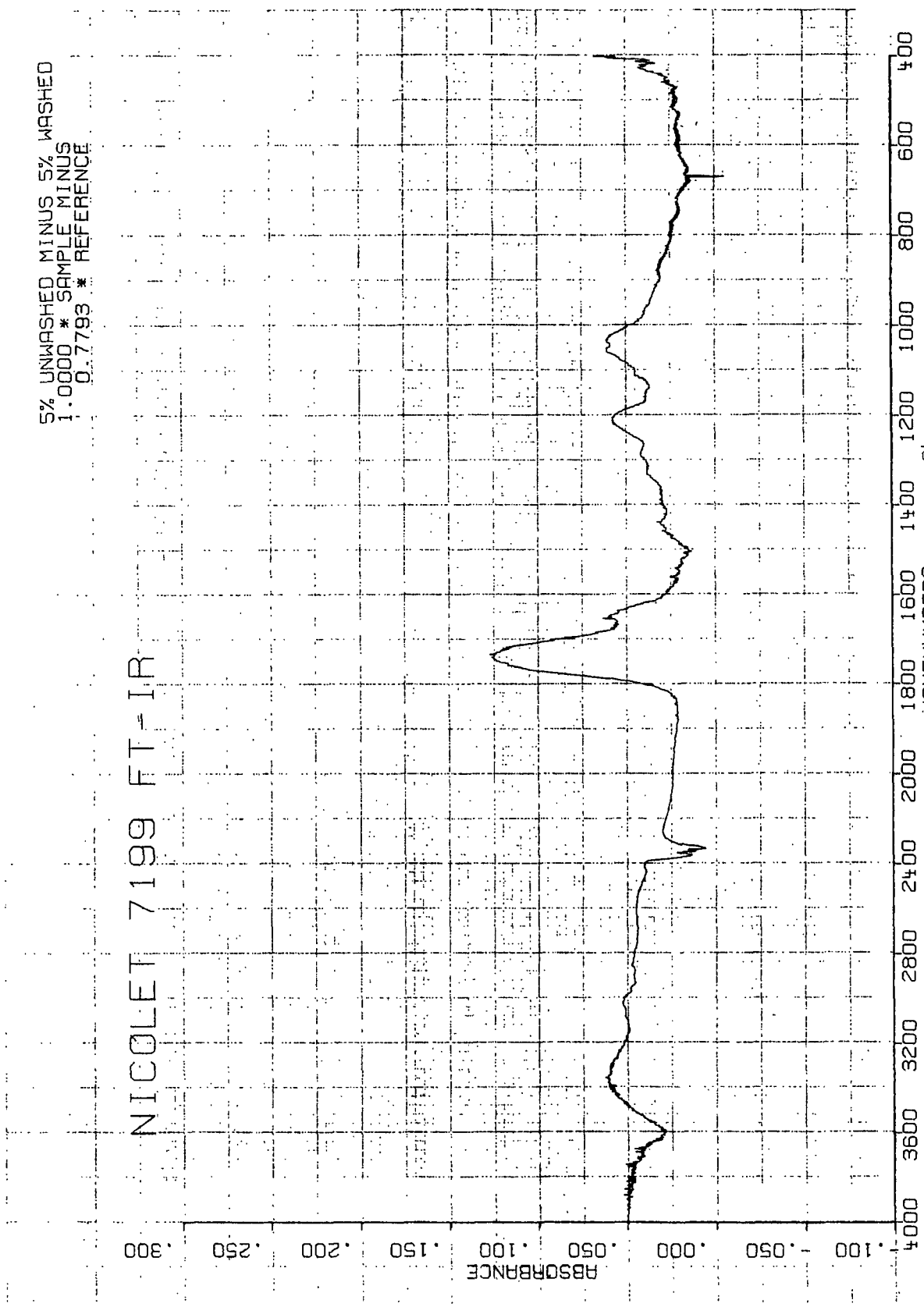

Figure 93. FT-IR Difference Spectrum of 5% Ozonized, Unwashed FW minus 5% Ozonized, Washed FW

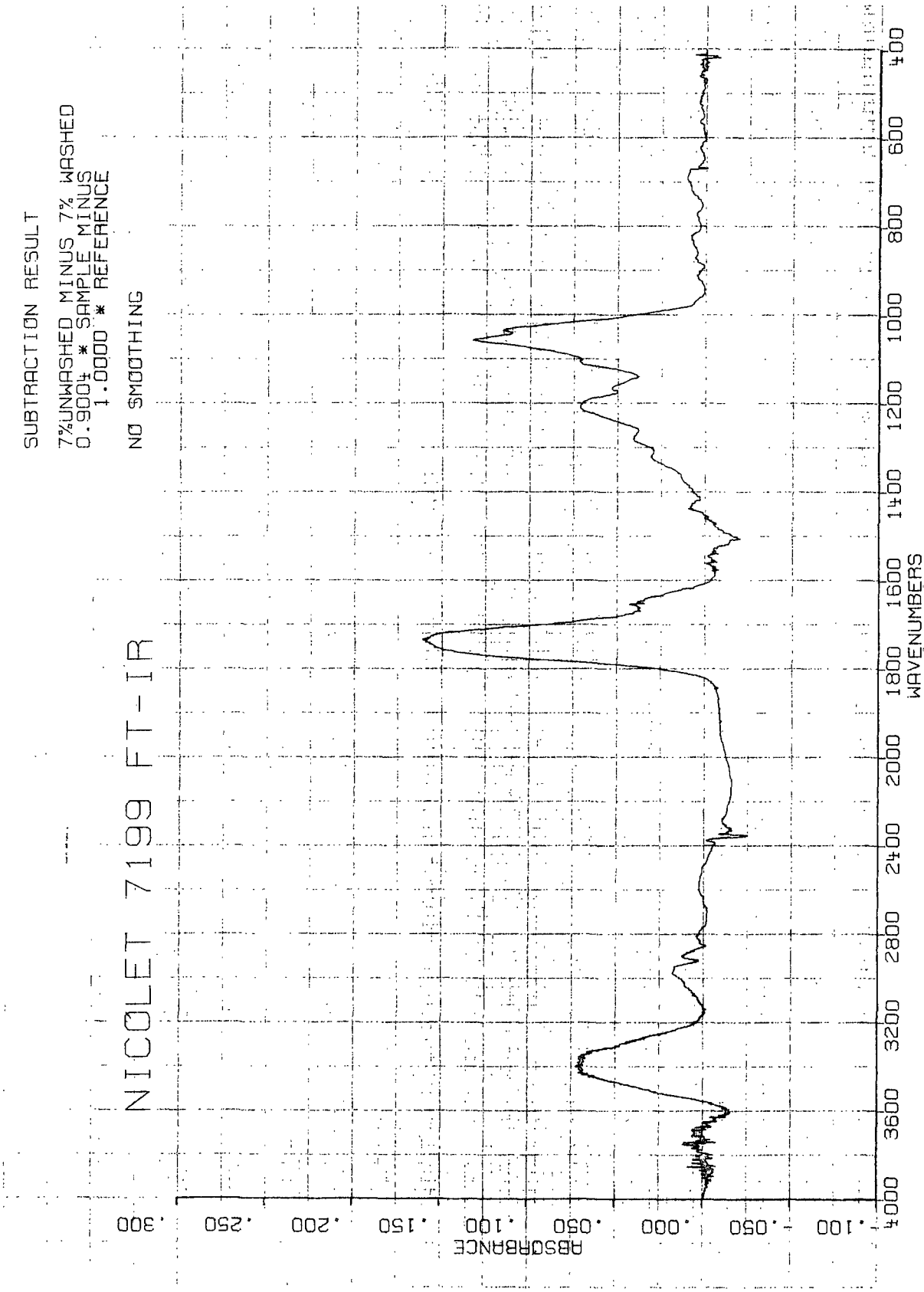

Figure 94. FT-IR Difference Spectrum of 7% Ozonized, Unwashed FW minus 7% Ozonized, Washed FW

APPENDIX VIII

OZONATED, NEUTRALIZED FIBERIZED WOOD FT-IR DIFFERENCE SPECTRA

The following FT-IR difference spectra were obtained, based on the transmission spectra given in Appendix V:

1. Ozonated, washed, neutralized FW minus untreated, neutralized FW

The difference spectra are given in Fig. 95-98.

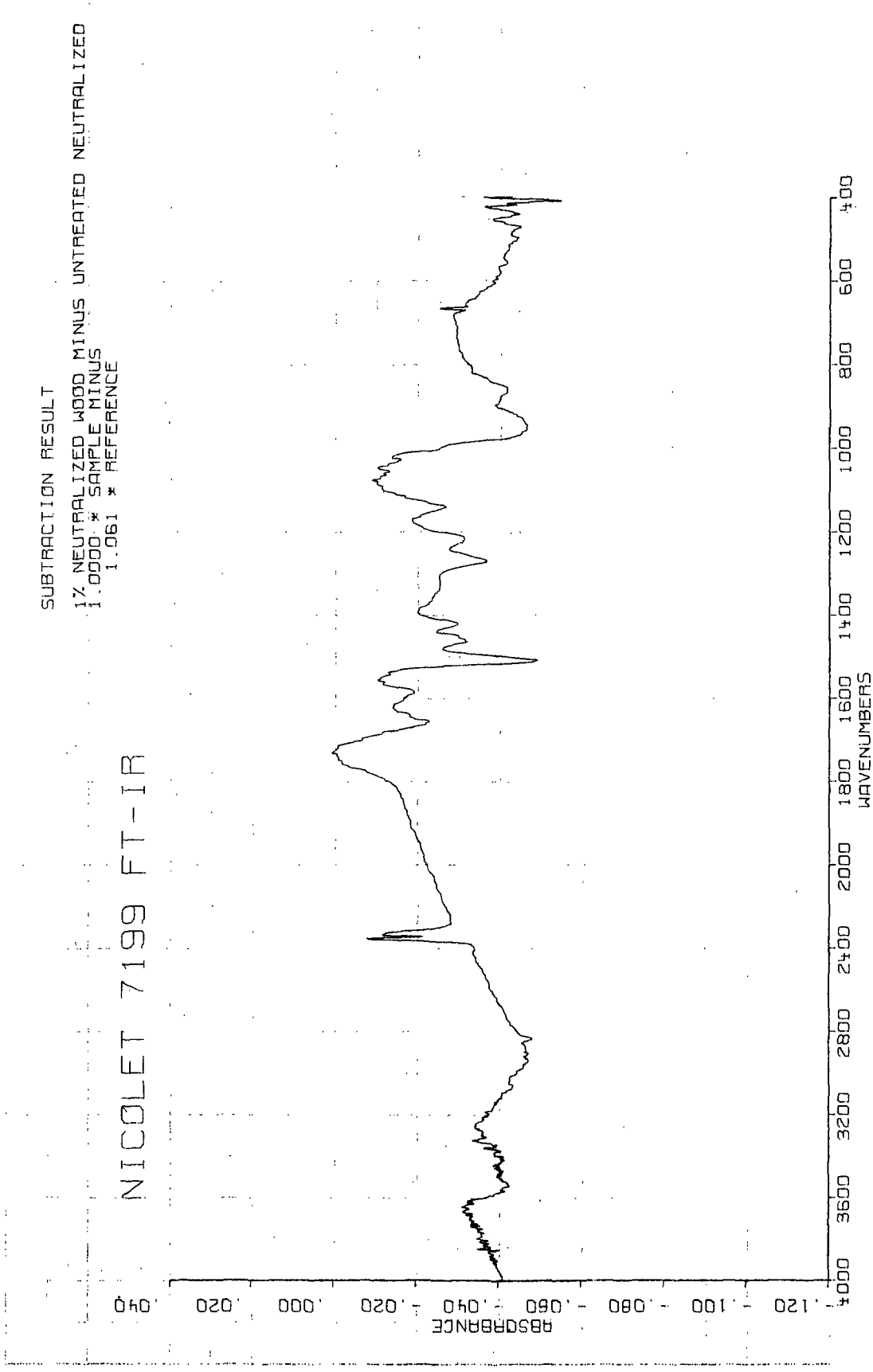

Figure 95. FT-IR Difference Spectrum of 1% Ozonized, Washed, Neutralized FW minus Untreated, Neutralized FW

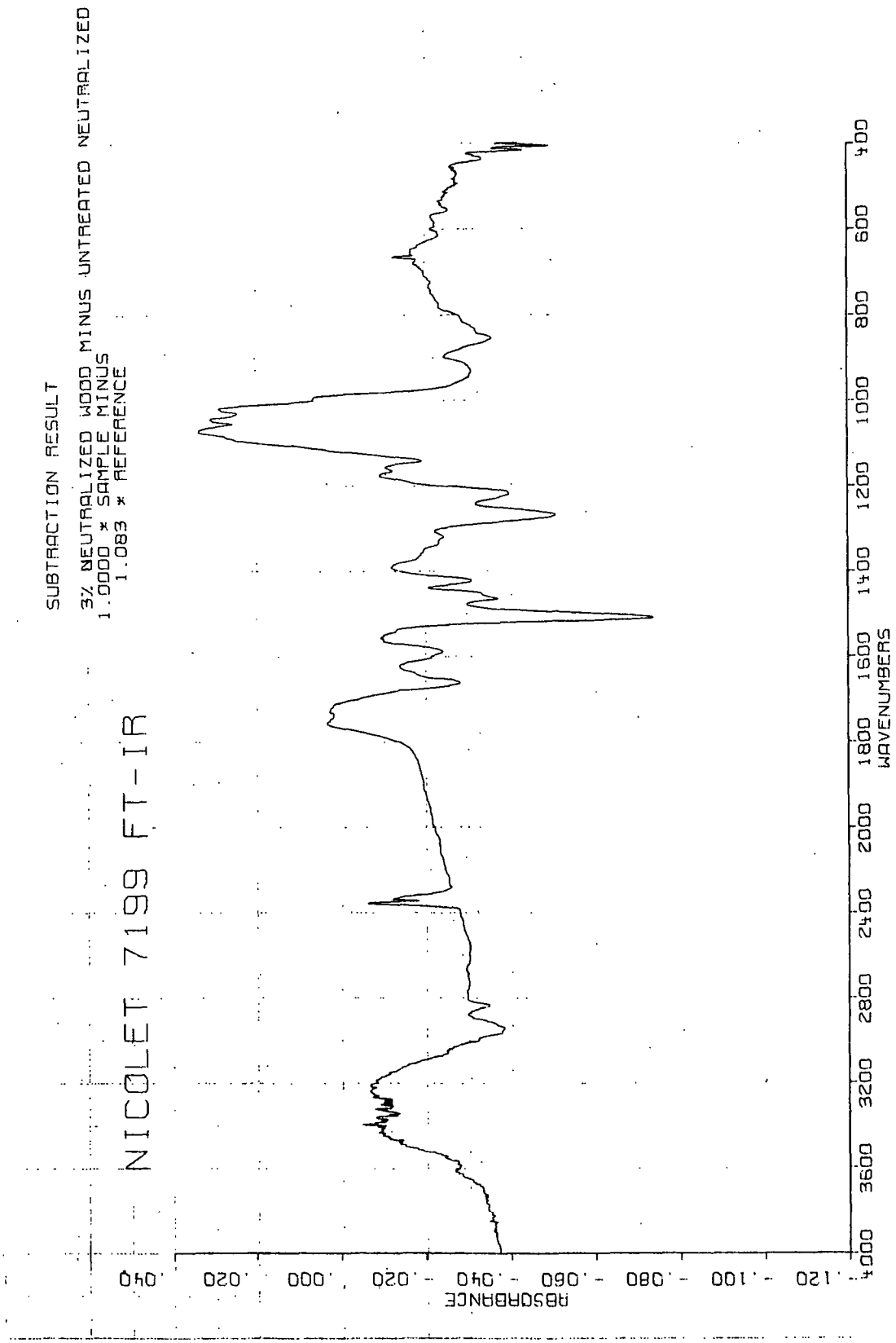

Figure 96. FT-IR Difference Spectrum of 3% Ozonized, Washed, Neutralized FW minus Untreated, Neutralized FW

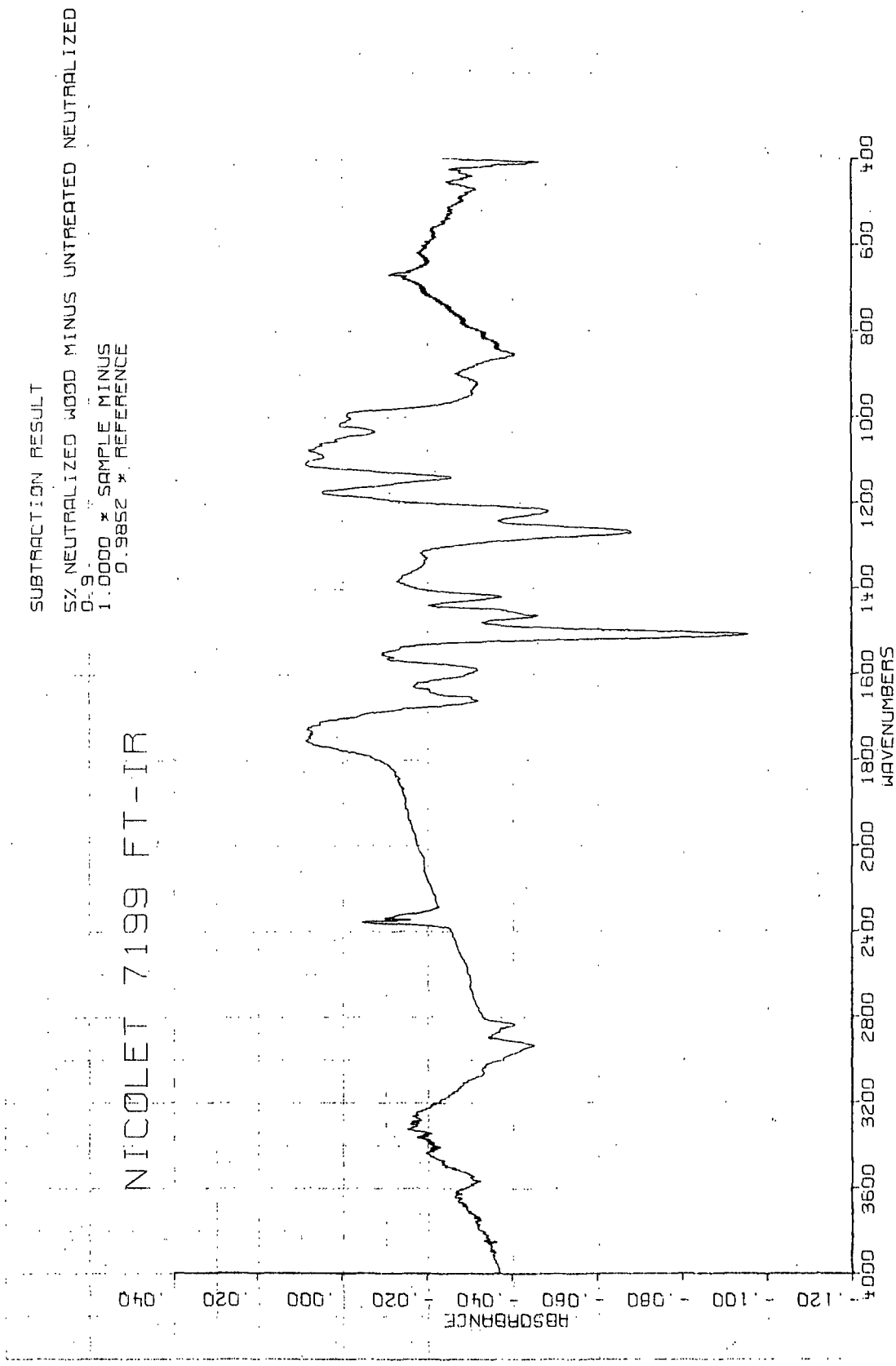

Figure 97. FT-IR Difference Spectrum of 5% Ozonized, Washed, Neutralized FW minus Untreated, Neutralized FW

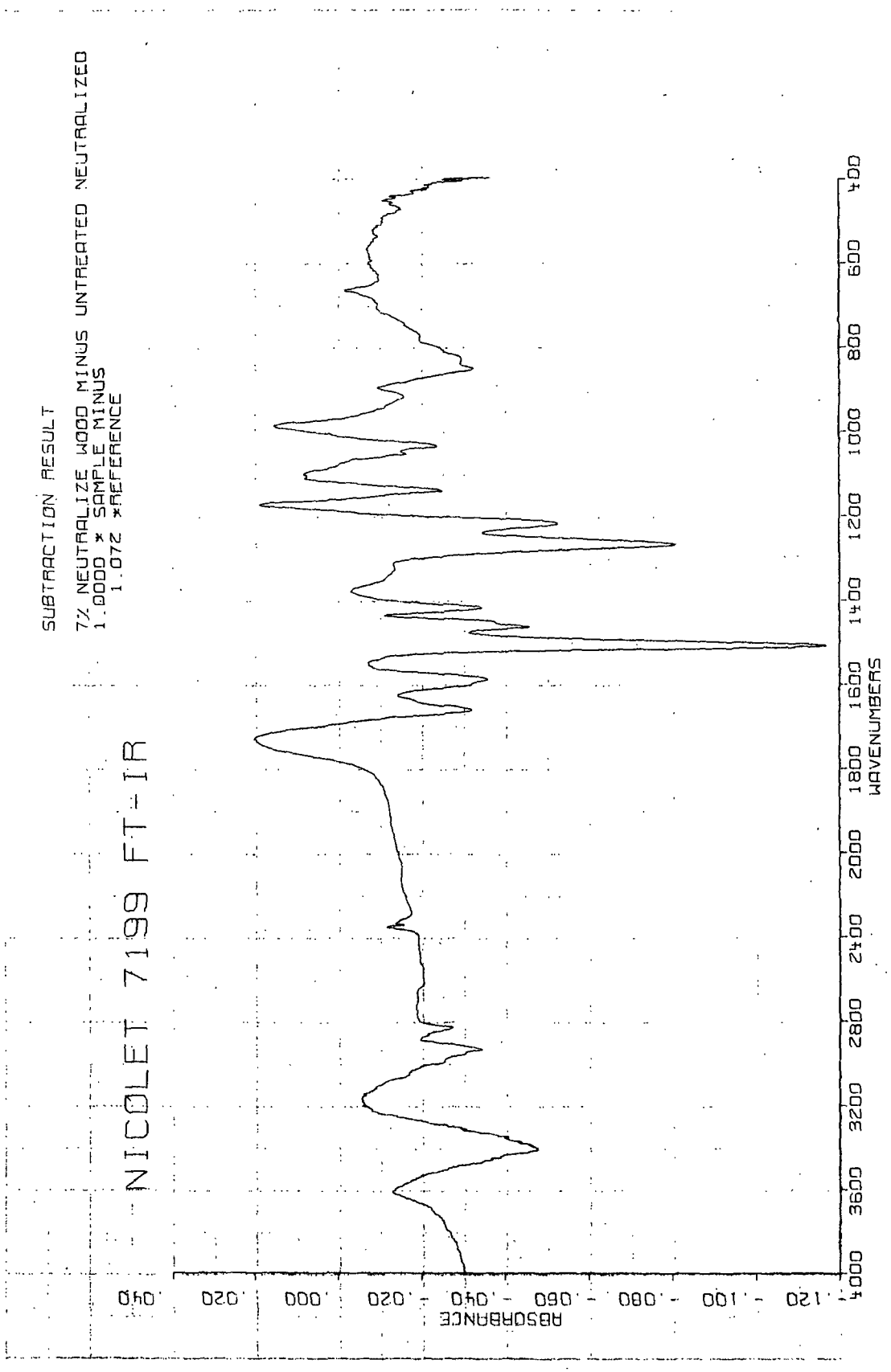

Figure 98. FT-IR Difference Spectrum of 7% Ozonized, Washed, Neutralized FW minus Untreated, Neutralized FW

APPENDIX IX

CALCULATION OF LIGNIN-FREE YIELD

The lignin-free yield of ozonated FW was calculated based on the total lignin contents (Klason + acid-soluble) and the washed yields determined for ozonated fiberized wood.

Basis: 1000 g untreated, oven-dry fiberized wood

In 1000 g FW there are 281 g lignin, and by difference, 719 g carbohydrate

At the 7% ozone level, the FW washed yield was 85.7% and the lignin content was 17.2%.

(1000 g FW)(0.857) = 857 g FW
(1000 g FW)(0.172) = 172 g FW Lignin
685 g carbohydrate in 7% ozonized, washed FW

Lignin-free yield (at 7% ozone) = (685 g/719 g) x (100) = 95.3%

APPENDIX X

EFFECT OF LIGNIN SOLUBILIZATION ON FIBERIZED WOOD BRIGHTNESS

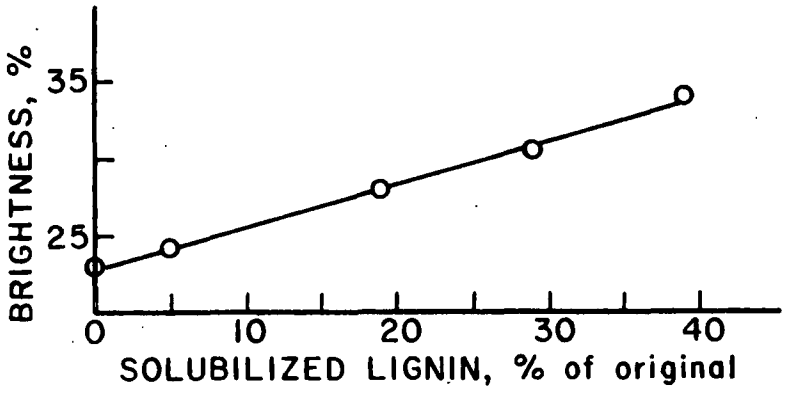

Figure 99. Brightness Versus Solubilized Lignin for Ozonated Fiberized Wood

APPENDIX XI

METHOXYL ASSOCIATED WITH LIGNIN IN FIBERIZED WOOD

The amount of methoxyl in FW that is associated with lignin was estimated. The calculation used to provide the estimate is shown below.

Assumption: The methoxyl content of the lignin in untreated FW is 16%

The total methoxyl content of untreated FW was found to be 4.85% and the total lignin content, 28.1%.

$$\frac{X}{28.1} = 0.16$$

where X = methoxyl content of lignin in FW; X = 4.50%.

$$\frac{4.50}{4.85} \times 100 = 93\%$$

Therefore, 93% of the methoxyl in untreated FW was associated with the lignin.

APPENDIX XII

METHOXYL CONTENT OF RESIDUAL LIGNIN IN OZONATED FIBERIZED WOOD

The methoxyl content of the residual lignin in ozonated FW was estimated. The calculation used to arrive at the estimate is given below.

Assumption: In ozonated FW, 93% of the methoxyl is associated with lignin

$$\frac{(0.93)\ M}{L} = \%\ \text{Methoxyl in ozonated FW lignin}$$

where M = methoxyl content of ozonated FW

L = residual lignin content of ozonated FW

APPENDIX XIII

METHOXYL CONTENT OF WATER-SOLUBILIZED MATERIAL

The methoxyl content of the water-soluble material removed during washing of ozonated FW was calculated. The calculation is based on methoxyl contents of untreated and ozonated FW and the washed yields determined for ozonated FW. An example of the calculation, for 1% ozonized FW, is given.

Basis: 1000 g oven-dry untreated fiberized wood

The methoxyl content of untreated FW = 4.85%

For 1% ozonized FW:

Washed yield = 98.8%

Methoxyl content = 4.58%

Thus, in

untreated FW	1000 g FW	48.5 g MeO
ozonated FW	-988 g FW	-45.8 g MeO
	12 g soluble material	2.7 g soluble methoxyl

$$\frac{\text{2.7 g soluble MeO}}{\text{12 g soluble FW material}} \times 100 = \underline{22.5\%}$$

Therefore 22.5% of the total solubilized material is methoxyl.

APPENDIX XIV

INFRARED SPECTRA OF ISOLATED REACTION PRODUCTS

The infrared transmission spectra of water-soluble reaction products isolated from 5 and 7% ozonized FW are shown in Fig. 100 and 101, respectively.

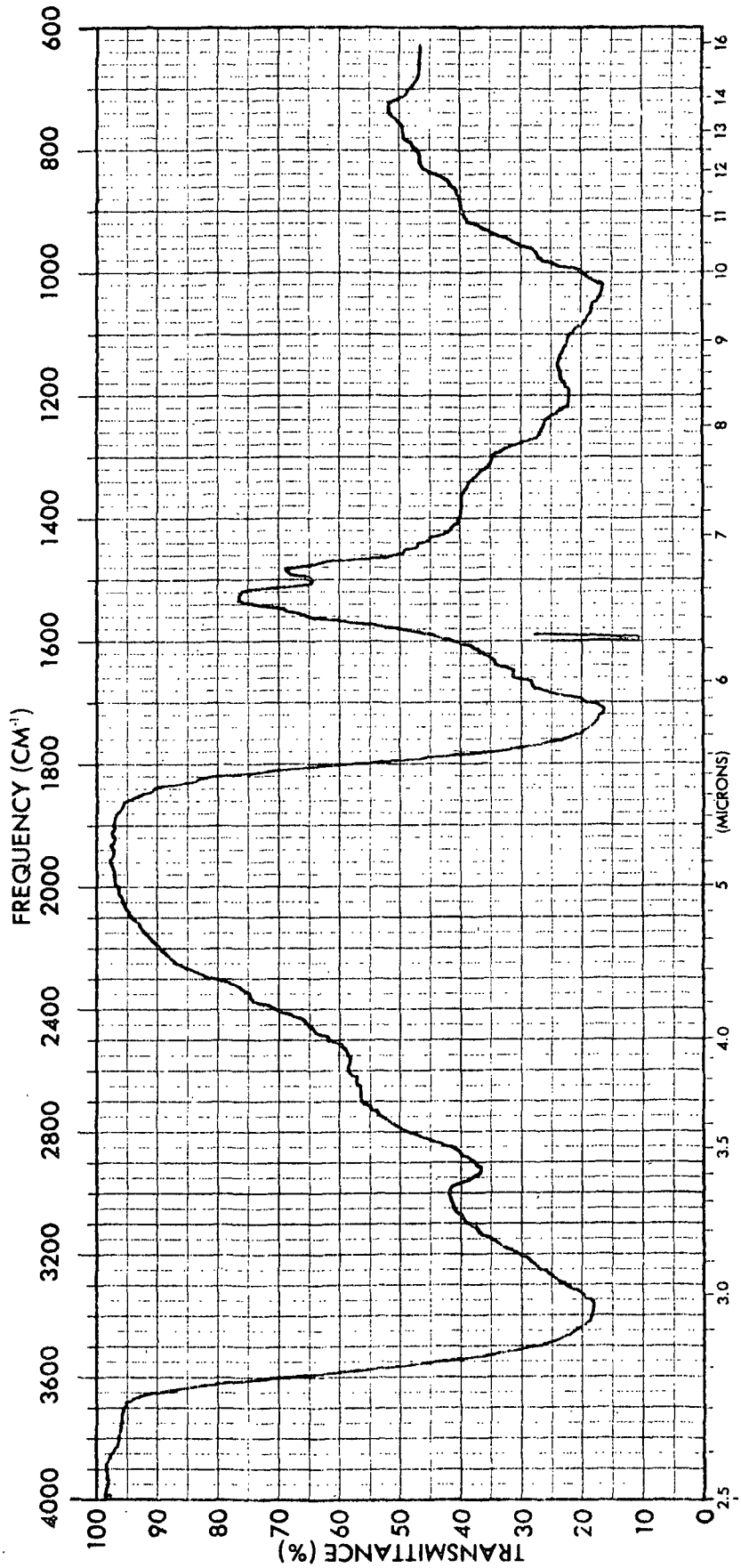

Figure 100. Infrared Transmission Spectrum of Isolated, Water-Soluble Reaction Products From 5% Ozonized Fiberized Wood

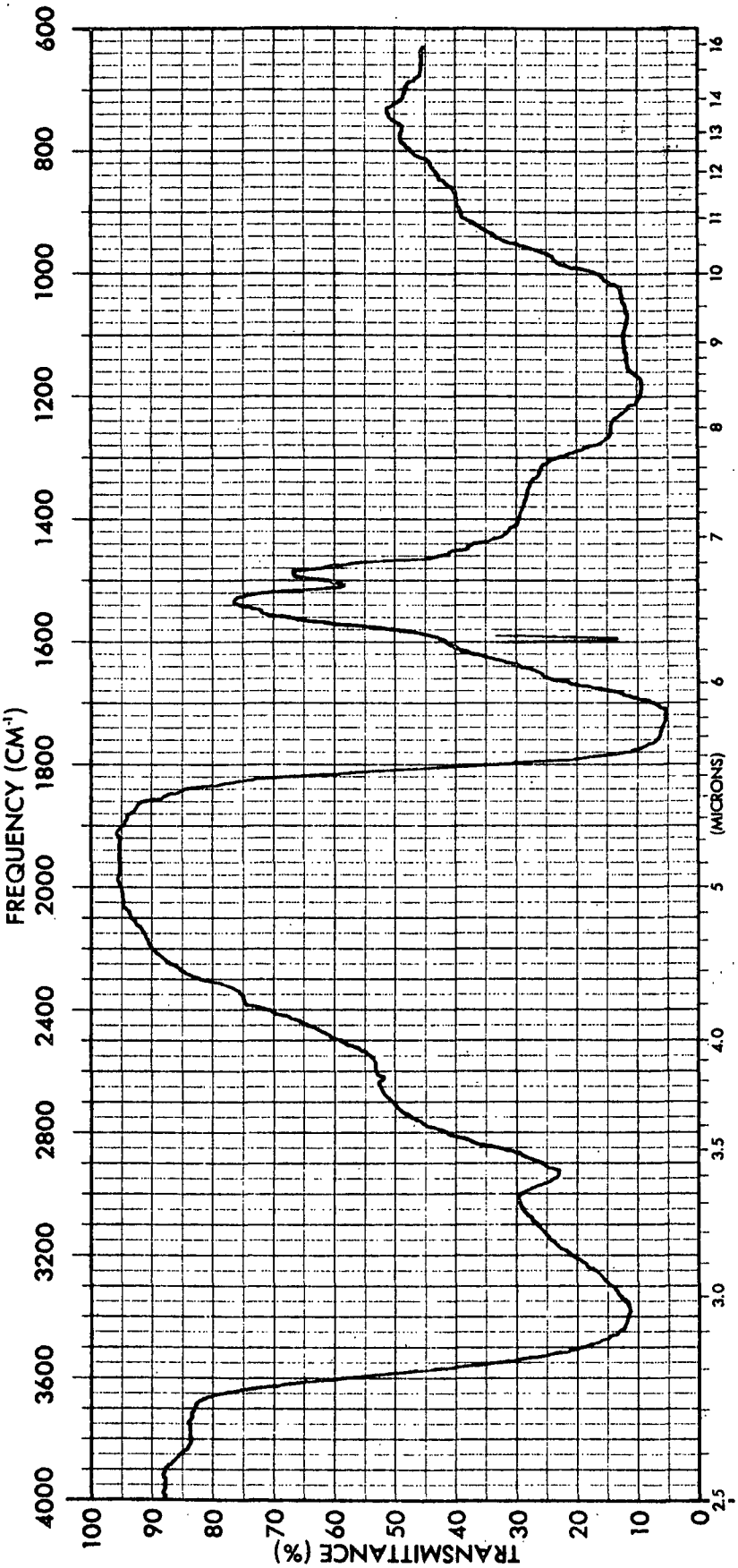

Figure 101. Infrared Transmission Spectrum of Isolated, Water-Soluble Reaction Products From 7% Ozonized Fiberized Wood

APPENDIX XV

NEUTRALIZED FW MINUS ACIDIFIED FW FT-IR DIFFERENCE SPECTRA

FT-IR difference spectra were obtained by subtracting acidified FW spectra (Appendix VI) from corresponding neutralized FW spectra (Appendix V). The results are shown in Fig. 102-106.

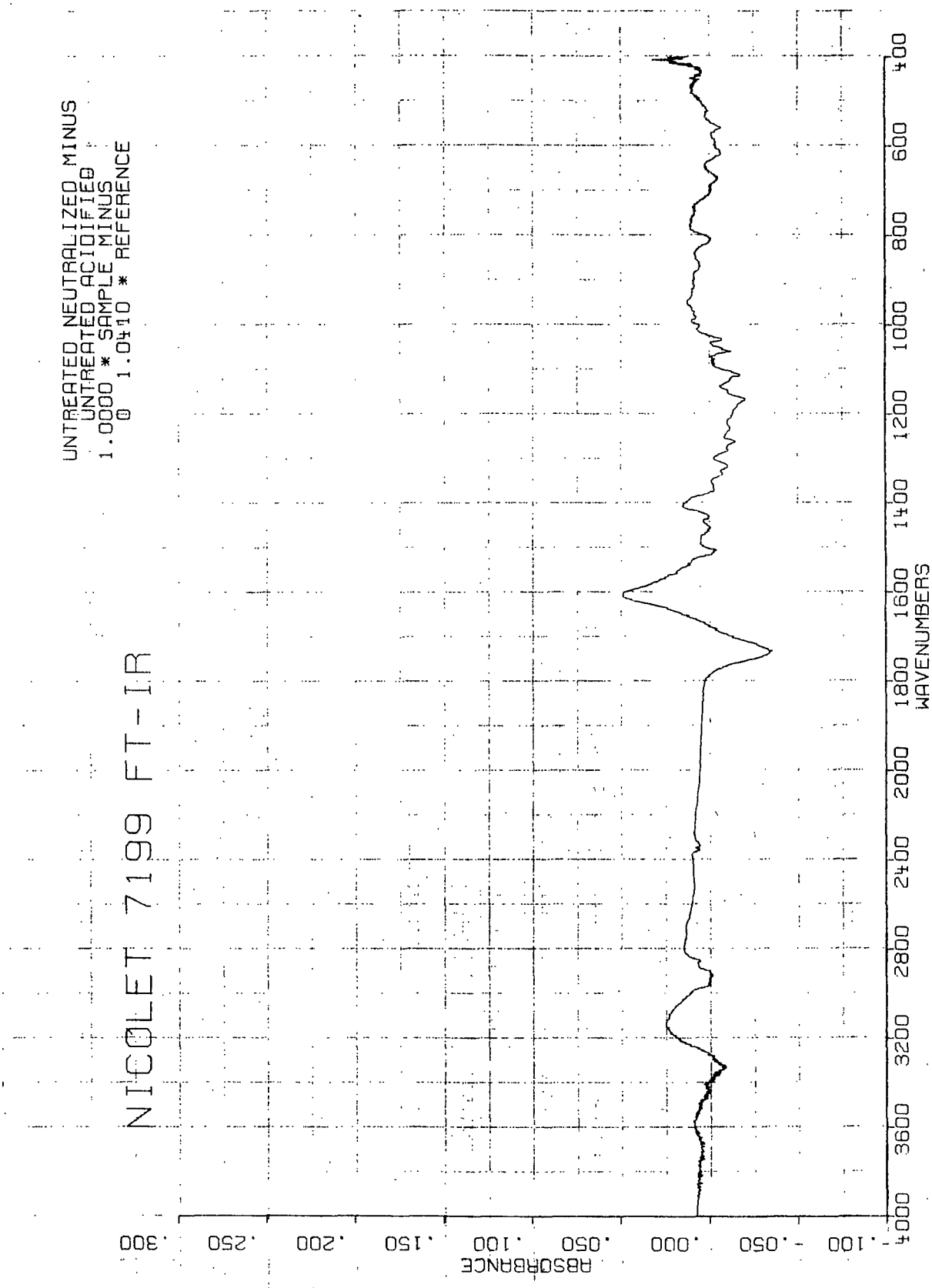

Figure 102. FT-IR Difference Spectrum of Untreated, Neutralized FW minus Untreated, Acidified FW

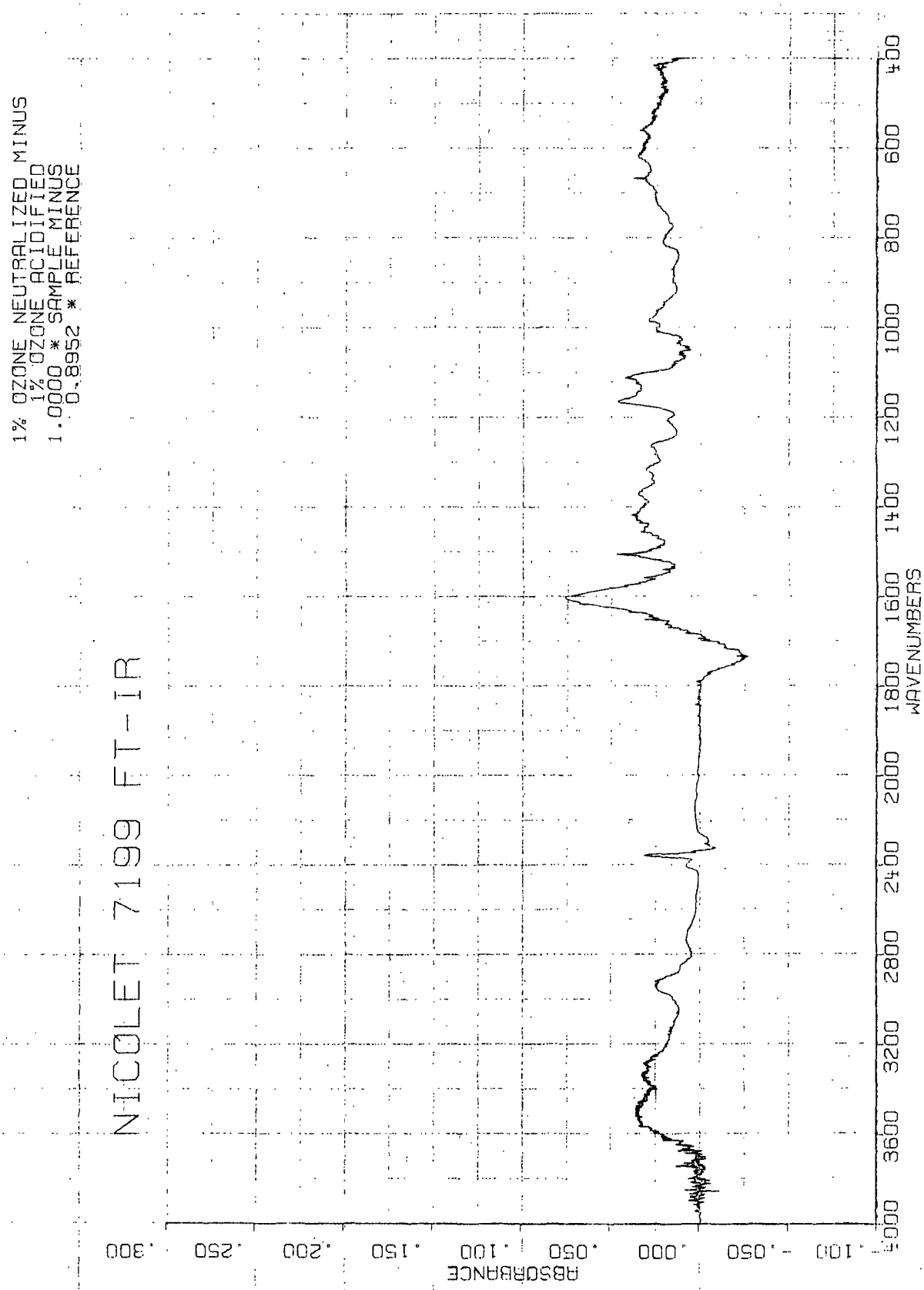

Figure 103. FT-IR Difference Spectrum of 1% Ozonized, Washed, Neutralized FW minus 1% Ozonized, Washed Acidified FW

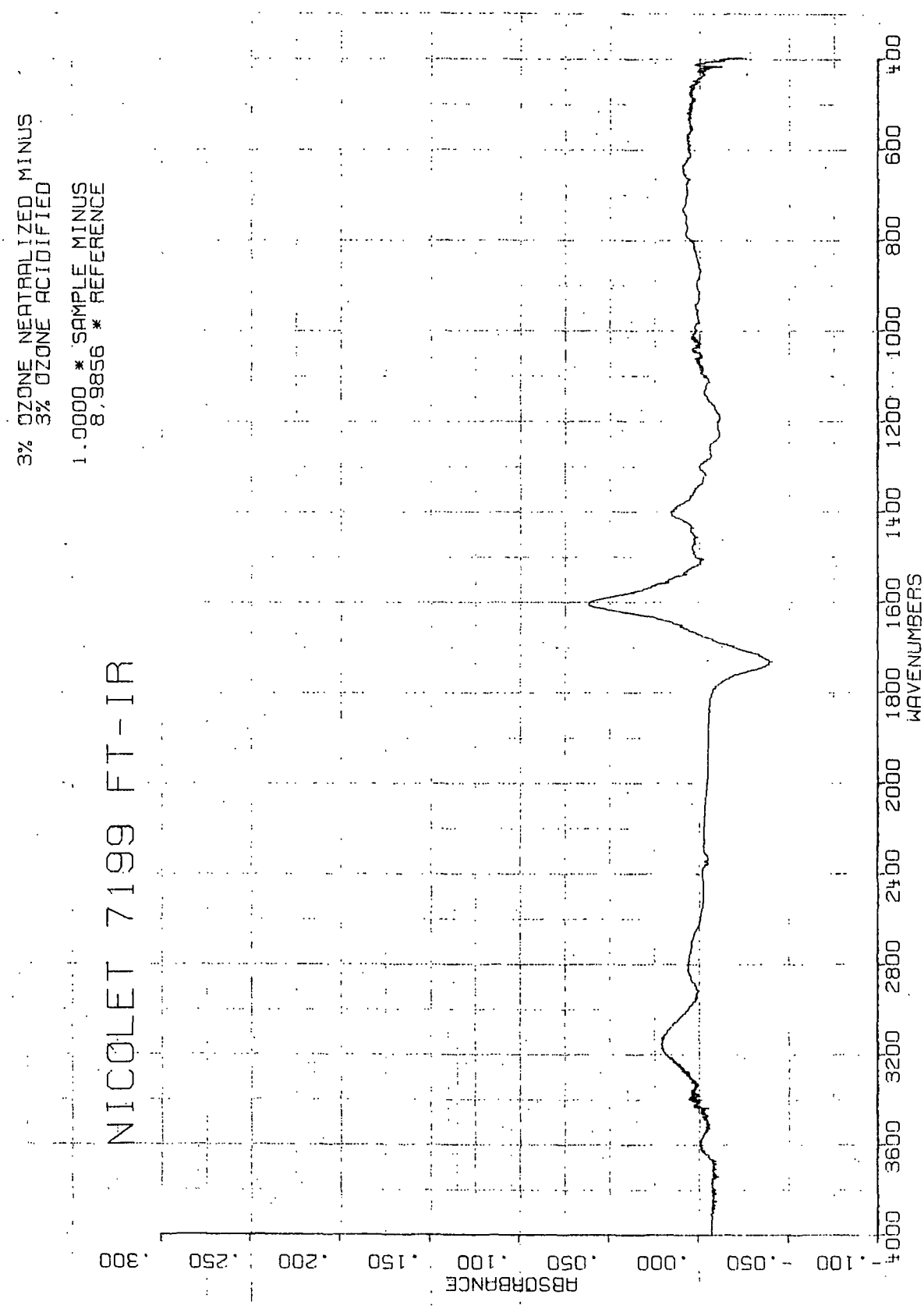

Figure 104. FT-IR Difference Spectrum of 3% Ozonized, Washed, Neutralized FW minus 3% Ozonized, Washed Acidified FW

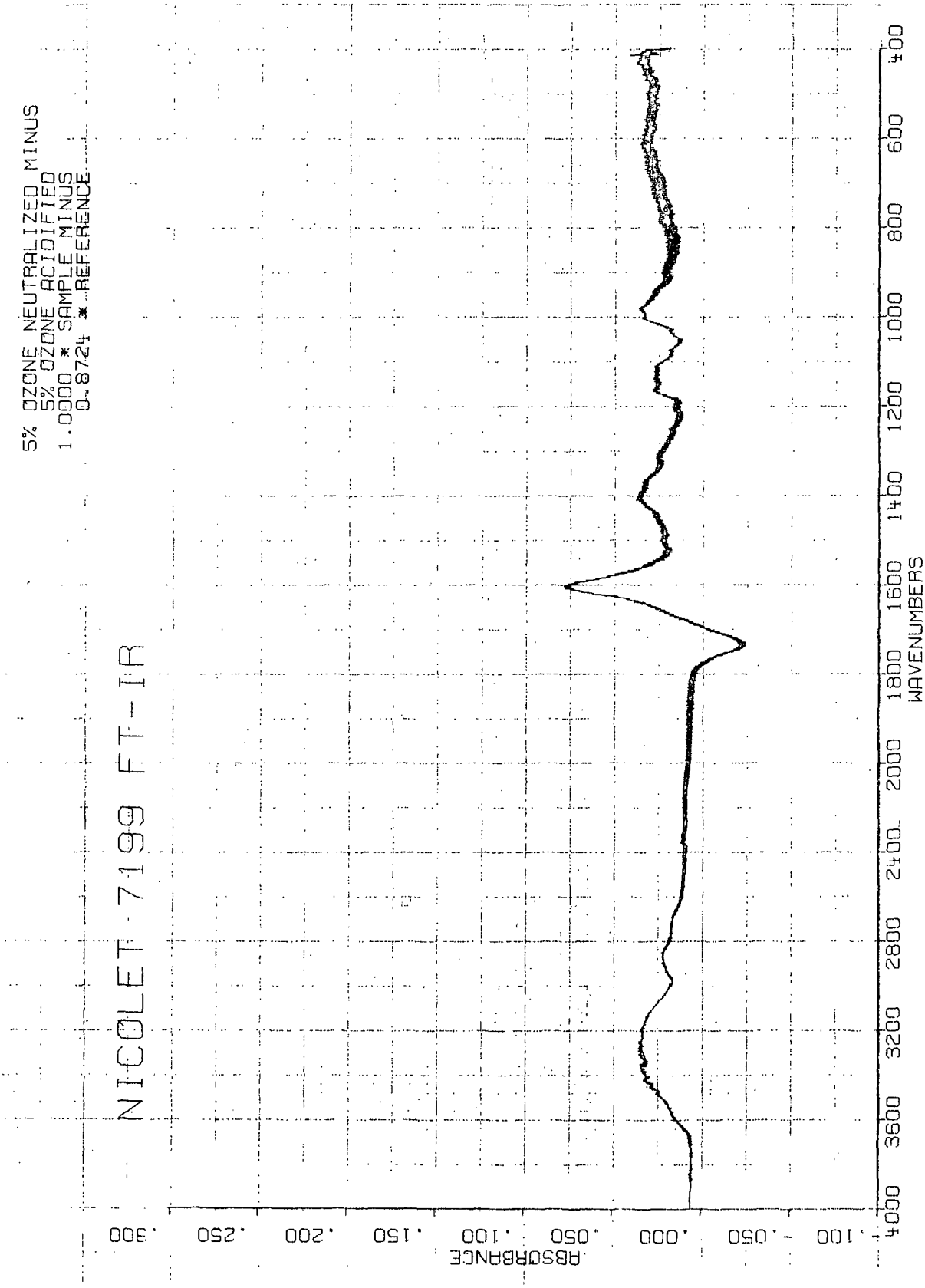

Figure 105. FT-IR Difference Spectrum of 5% Ozonized, Washed, Neutralized FW minus 5% Ozonized, Washed Acidified FW

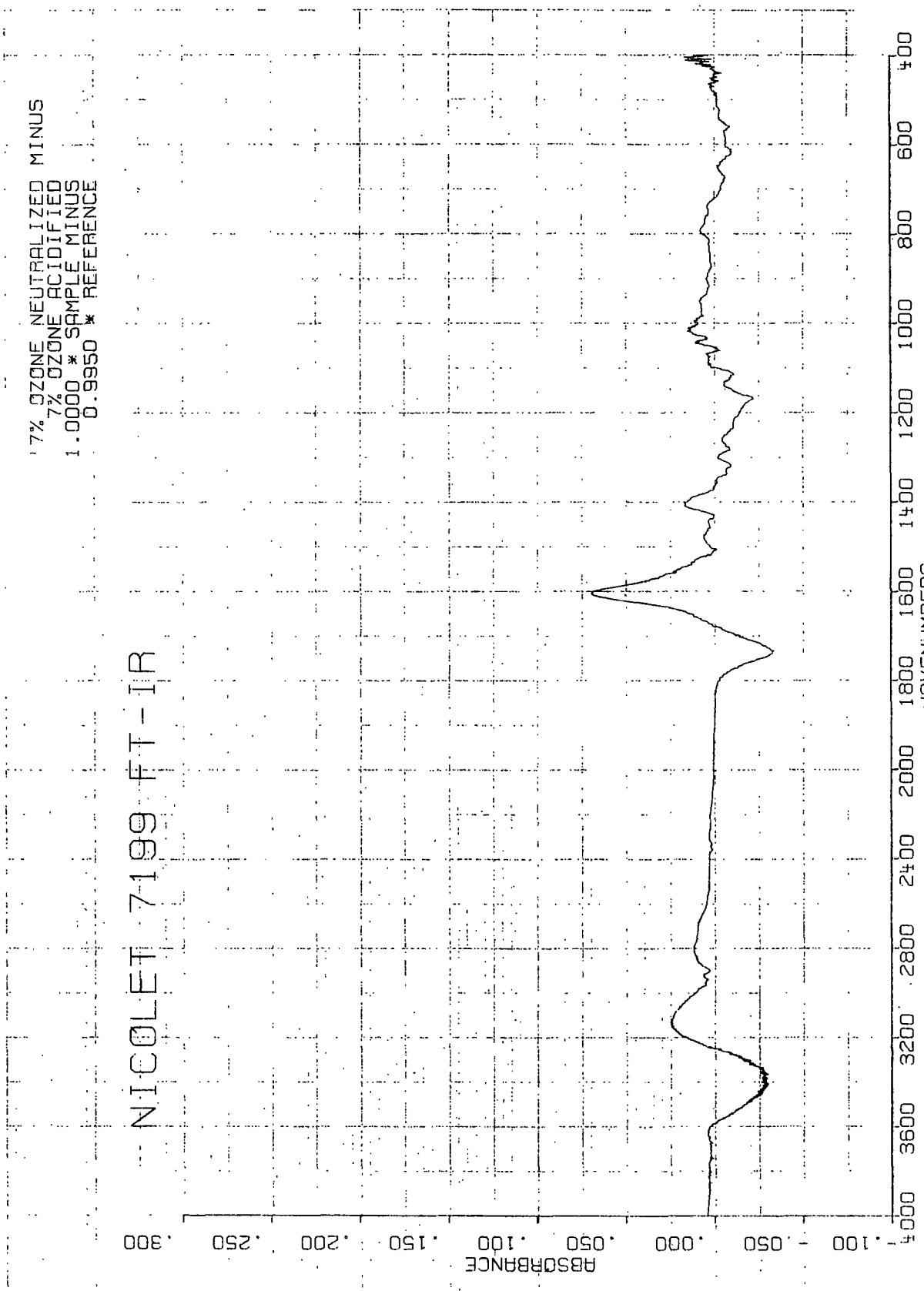

Figure 106. FT-IR Difference Spectrum of 7% Ozonized, Washed, Neutralized FW minus 7% Ozonized, Washed Acidified FW

APPENDIX XVI

INFRARED SPECTRA OF HOLOCELLULOSE ISOLATED FROM UNTREATED AND OZONATED FIBERIZED WOOD

The infrared transmission spectra of holocellulose samples isolated from untreated and ozonated FW are shown in Fig. 107-109.

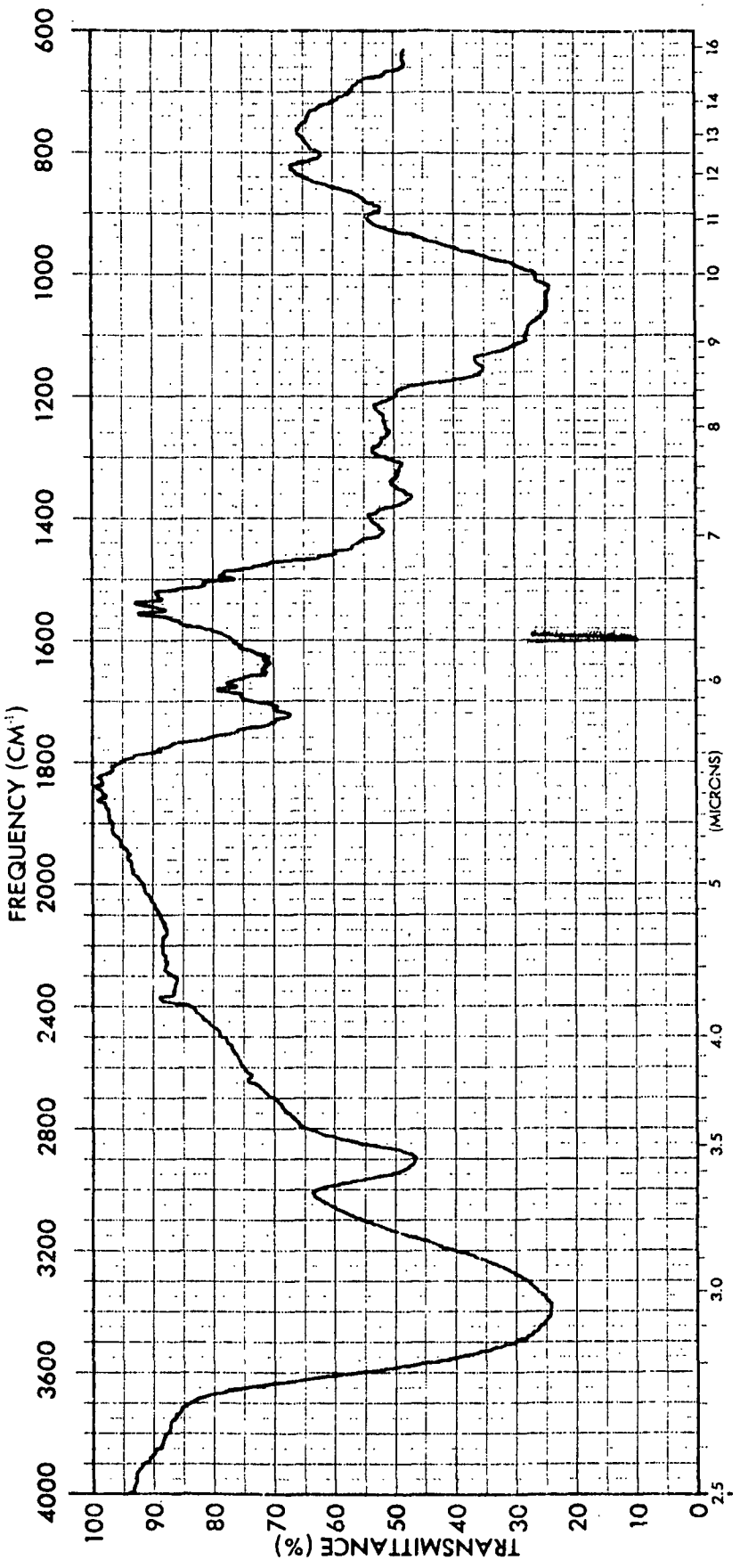

Figure 107. Infrared Transmission Spectrum of Holocellulose Isolated From Untreated FW

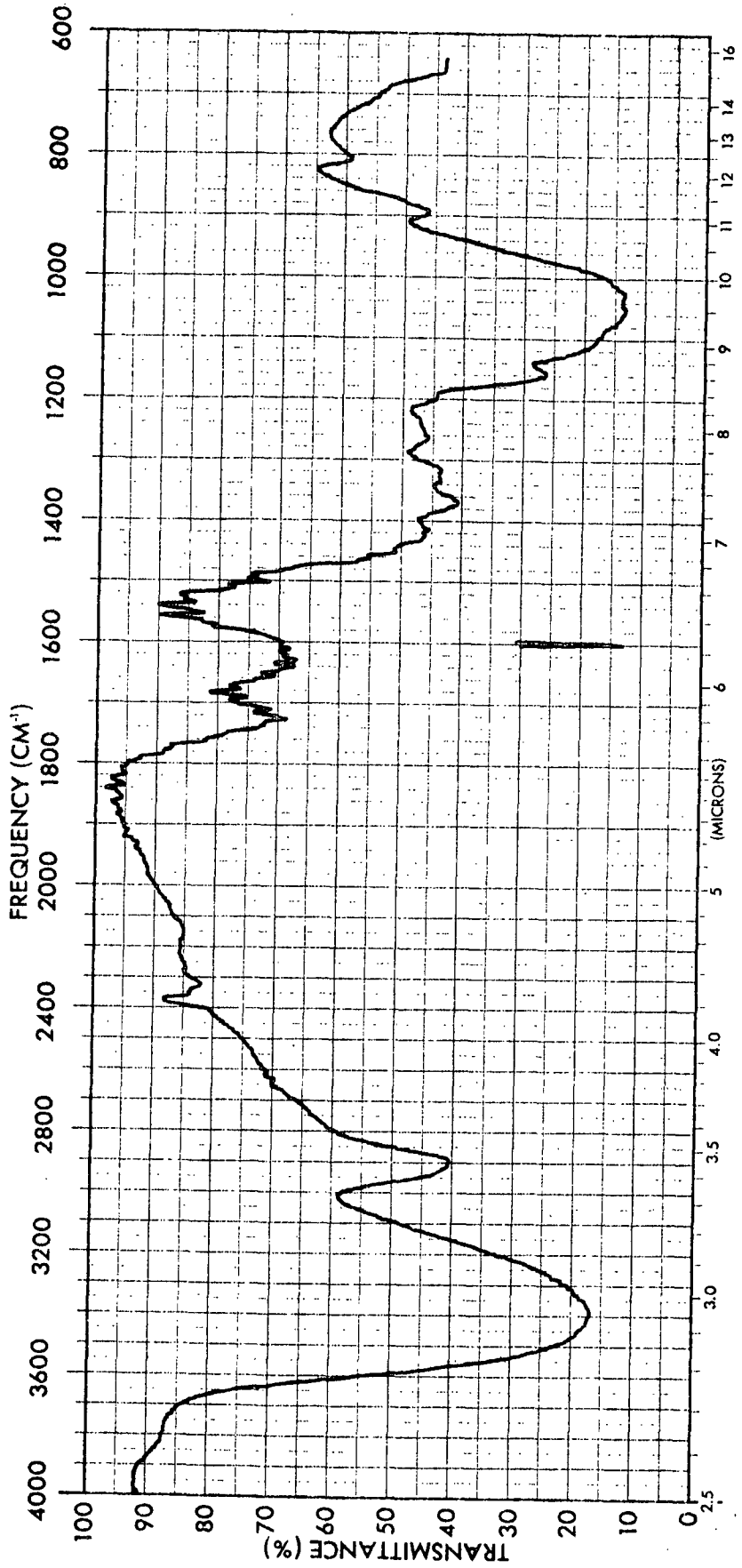

Figure 108. Infrared Transmission Spectrum of Holocellulose Isolated From 3% Ozonized FW

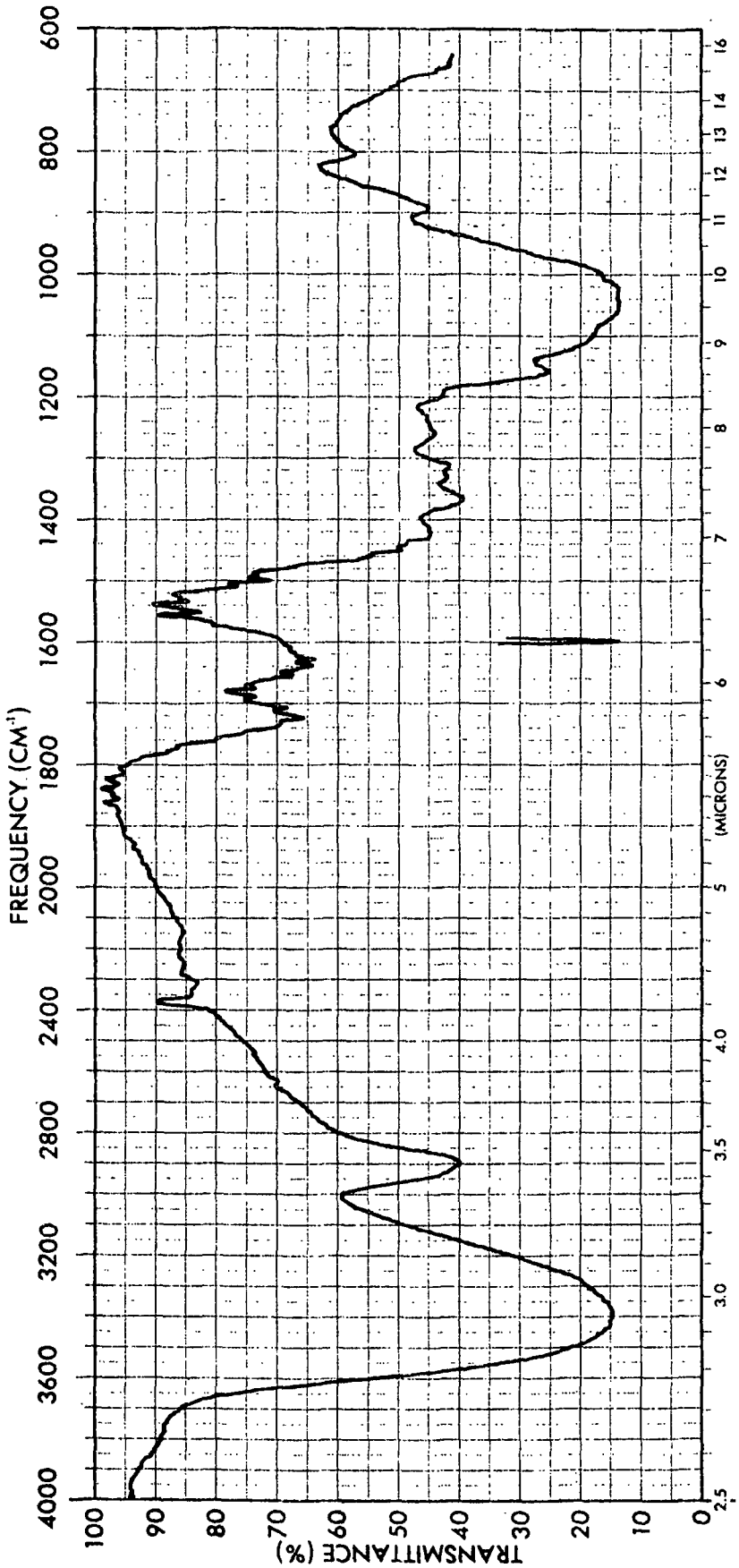

Figure 109. Infrared Transmission Spectrum of Holocellulose Isolated From 5% Ozonized FW

APPENDIX XVII

INFRARED SPECTRUM OF LOBLOLLY PINE DIOXANE LIGNIN

The infrared transmission spectrum of loblolly pine dioxane lignin obtained by Crozier (53), is shown in Fig. 110.

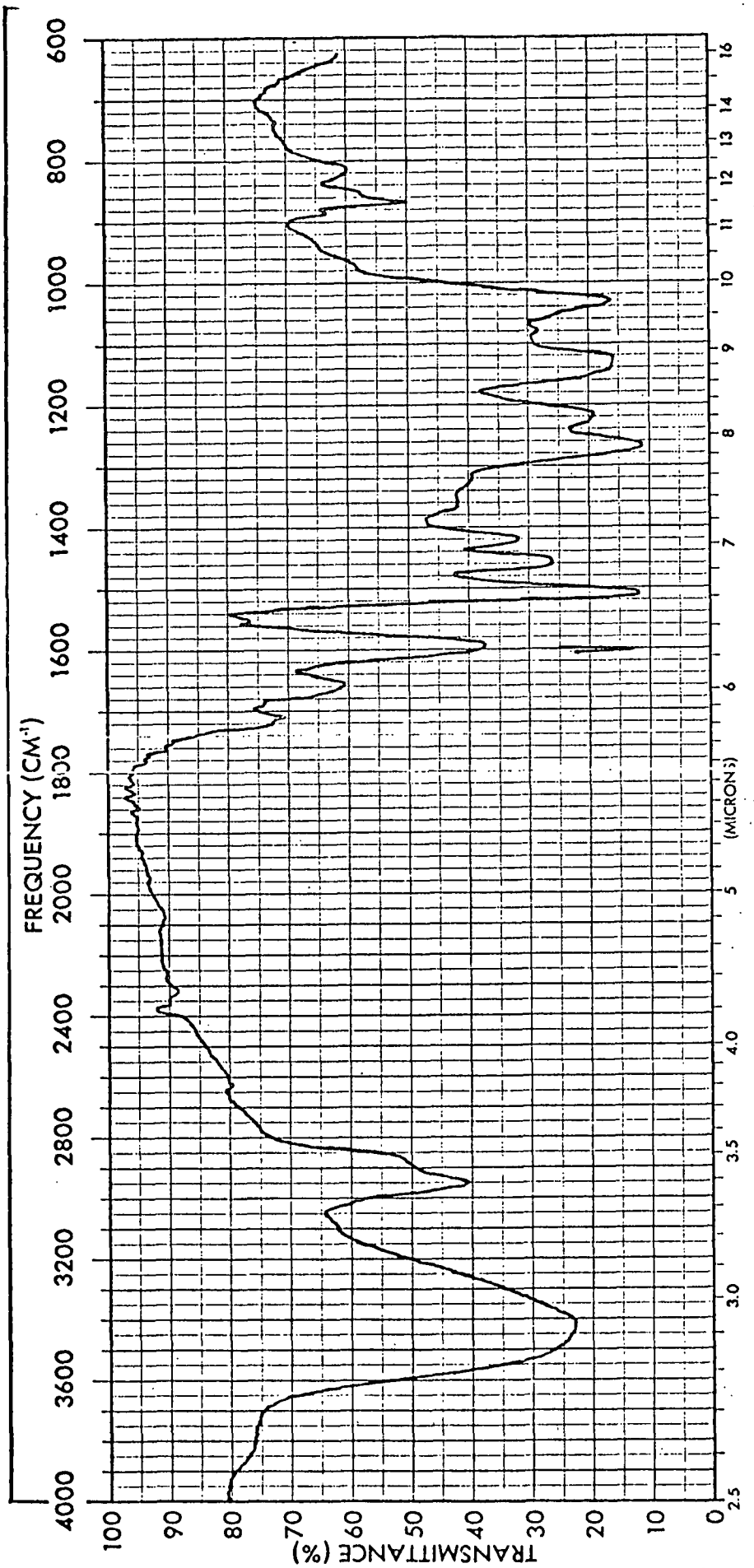

Figure 110. Infrared Transmission Spectrum of Loblolly Pine Dioxane Lignin (54)

APPENDIX XVIII

PHENOLIC HYDROXYL CONTENT OF FW BASED ON METHYLATION RESULTS

The phenolic hydroxyl content of untreated and ozonated FW was estimated. The estimates were based on methylation results obtained for FW and cotton cellulose. An example of the calculation used to estimate phenolic hydroxyl content is given below.

Assumptions:

1. The methoxyl content of untreated FW lignin is 16%.
2. In ozonated FW, 93% of the methoxyl is associated with the lignin (based on a previous calculation for untreated FW, Appendix XVI).
3. There are methoxyl groups present on 96% of the lignin monomers in FW (54).

Basis: 1000 g of ozone-treated, washed oven-dry fiberized wood

Example of calculation for 3% ozone-treated FW:

Total lignin content	= 24.4%	= 244 g
Holocellulose content	= 75.6%	= 756 g
Initial methoxyl content	= 4.19%	= 41.9 g
Final methoxyl content	= 5.17%	= 51.7 g

Note: Values are not corrected for washed yield.

The initial methoxyl content is multiplied by 0.93 to give the methoxyl associated with lignin: (41.9 g MeO)0.93 = 39.0 g MeO in FW lignin.

By difference there is 41.9 — 39.0 = 2.9 g MeO in FW holocellulose.

It was found that methylation increased the methoxyl content of cellulose by 3.2 g/1000 g o.d. cellulose. Applying this increase to holocellulose of FW gives:

$$\frac{3.2 \text{ g MeO}}{1000 \text{ g cellulose}} = \frac{x}{756 \text{ g holocellulose}}$$

x = 2.4 g increase in methoxyl content of holocellulose following methylation

Therefore, the total methoxyl content of FW holocellulose in methylated FW is:

2.4 g (increase) + 2.9 g (initial amount) = 5.3 g methoxyl

Subtracting this amount from the total amount of methoxyl in methylated FW gives the amount of methoxyl present in the lignin of methylated FW.

51.7 g - 5.3 g = 46.4 g methoxyl in methylated FW lignin

The phenolic hydroxyl content, based on the initial and final methoxyl contents of FW lignin, can now be calculated using the equation shown below,

$$\frac{(M_f - M_i)\ 0.96}{M_i} \times 100 = \text{PhOH (\#/100 lignin monomers)},$$

where M_i = initial methoxyl content of FW lignin

M_f = final methoxyl content of FW lignin

0.96 = represents the fact that 96% of the lignin monomers contain a methoxyl group

Using the previously obtained values and the equation given above:

$$\frac{(46.4 - 39.0)(0.96)}{39.0} \times 100 = \underline{18.2}$$

Thus, there are 18.2 phenolic hydroxyl groups/100 lignin monomers in 3% ozone-treated FW.